Reactions and Co-ordination Chemistry of Indium Trialkyls and Trihalides.

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A thesis submitted for the degree of Doctor of Philosophy.

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To Mam and Dad

-for making this possible.

Contents.

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Diagrams and Tables.

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Declaration.

All of the work described in this thesis is original and was, except where otherwise indicated, carried out by the author.

Ian A. Degnan
(September 1989)

Some of the work desribed in this thesis has been published in the following reference.

N. W. Alcock, I. A. Degnan, M, G. H. Wallbridge, H. R. Powell, M. McPartlin, G. M. Sheldrick, *J. Organomet. Chem.*, 1989, **361**, C33.

Abbreviations.

Ölander numbering is used throughout for the groups of the periodic table.

DMSO	Dimethylsulphoxide
L	Ligand
X	Halide
R	Alkyl group
Cy	Cyclohexyl
Ph	Phenyl
Me	Methyl
Et	Ethyl
Bu^t	*t*-Butyl
Bu^i	*i*-Butyl
Pr^i	*i*-Propyl
Bu^n	*n*-Butyl
Sal	Salicylaldehyde
Py	Pyridine
Diphos	bis-1,2-diphenylphosphinoethane.
acac	Acetylacetonate
THF	Tetrahydrofuran
TMEDA	Tetramethylethane-1,2-diamine
vs	very strong
s	strong
m	medium
w	weak
vw	very weak
sh	shoulder
br	broad
N.m.r.	Nuclear magnetic resonance
N.Q.R.	Nuclear Quadrupolar Resonance.
E. I.	Electron impact.
C. I.	Chemical ionisation
G. C.	Gas chromatography
D	dimer
M	monomer
M. Pt.	melting point

Summary.

This thesis describes a broad study of the co-ordination chemistry and reactions of indium trihalides and trialkyls. Particular emphasis has been placed upon indium compounds which also contain phosphorus.

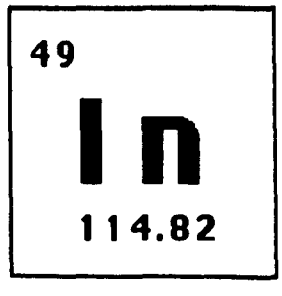
A detailed study of the 1:1 complexes formed between indium triiodide and several phosphine ligands is described. *X*-ray crystallographic studies showed that these complexes are tetrahedral monomers in the solid state. This is the first conclusive proof that indium triiodide will form monomeric tetrahedral complexes. N.m.r. studies have also been carried out on these complexes. Also described are the results of *X*-ray diffraction studies on two other phosphine complexes, $InCl_3(PMe_3)_2$ and $(InI_3)_2(Diphos)_3$. The latter complex is the first example of a trigonal bipyramidal structure that has been reported for any indium triiodide complex.

The reactions between methyllithium and two indium triiodide-phosphine complexes are described. This proved to be a useful method for preparing methylated derivatives of these complexes. The reactions between indium triiodide and $LiPBu^t_2$ are also described. Three equivalents of this reagent yielded $In(PBu^t_2)_3$, which was shown by *X*-ray crystallography to be an example of a rare monomeric three co-ordinate indium compound.

Also described in this thesis are the preparations of several novel organoindium derivatives by the reaction of either trimethyl- or triethylindium with acidic compounds containing protonic hydrogens. Where possible, structures of the products of these reactions have been deduced. One of these compounds $[(Et_2InPBu^t_2)_2]$ was studied in greater detail and in the solid state it was shown by *X*-ray crystallography to be dimeric. Its thermal decomposition was also studied in view of the possible relevance of such compounds to the preparation of indium phosphide. Possible decomposition pathways are discussed.

CHAPTER 1

INTRODUCTION



There is a great deal of topical interest in the chemistry of the group 13 elements. One of the reasons for this is the use of some of their compounds in the preparation of semi-conducting materials such as indium phosphide and gallium arsenide (the so called III-V semi-conductors). Consequently much of the recent work in this area that has been carried out has been concentrated on the chemistry of compounds which may be of use as precursors in the preparation of these semi-conductors. Such compounds fall into two types. Firstly, those which can act as a source of only one of the required elements and so need to be used in the presence of another compound which can act as the source of the other element (examples are $GaMe_3$, $InMe_3$, PH_3 and AsH_3). The second type of compound is those which can act as a source of both of the required elements, that is, they contain both a group 13 and a group 15 element (an example is $[Me_2InPBu^t_2)_2]$).

A hindrance to further developments in this area is our poor understanding of the chemistry and properties of such compounds. This is particularly true of the compounds of indium. Until the 1960's this element was both difficult to obtain and expensive and so research into its chemistry was very limited. Since then, improved refining techniques and increased production have led to it being more readily available.

Despite this, however, indium remains one of the less well studied elements with many questions concerning the chemistry of its compounds still unanswered. This applies not only to compounds of relevance to the preparation of semi-conductors but to the chemistry of its compounds in general. One particular area of note is the co-ordination chemistry of the indium trihalides. Very little is known about the solid state structures or solution behaviour of their complexes.

In particular the sparsity of *X*-ray crystallographic studies and n.m.r. studies are particular barriers to advancements in these areas.

In view of these points it was decided to carry out a study of the co-ordination chemistry and reactions of compounds of indium with a particular emphasis on preparing and studying compounds which also contain phosphorus. Phosphorus was chosen because indium phosphide is currently one of the more important indium containing semi-conductors and also because of the ready availability of a wide variety of phosphorus containing compounds.

As mentioned above, the most important industrial application of indium compounds is as precursors in the preparation of semi-conductors. One of the industrial processes used is known as metallo organic vapour phase epitaxy (MOVPE). This normally involves the thermal decomposition of an indium trialkyl compound (commonly $InMe_3$). This is discussed in more detail in Chapter 5 (page 161). For this process, very high purity indium compounds are essential. A method of achieving this degree of purity is to form a complex between the indium trialkyl and a phosphorus containing ligand and then to regenerate the indium compound by "cracking" the complex. This has the effect of removing the majority of the impurities. After "cracking", the main impurity is the ligand that was used to form the complex. As the desired semi-conductor is indium phosphide, the presence of a trace of a phosphorus containing impurity such as this ligand in the indium trialkyl compound is usually acceptable.

It has recently been shown that indium phosphide can also be prepared in this process from a precursor that contains both indium and phosphorus ($[Me_2InPBu^t_2]_2$).[1] This is discussed in more detail in Chapter 5 (page 161).

Of specific industrial interest, therefore, is the preparation of alkyl indium compounds, their co-ordination chemistry, reactions with phosphorus containing ligands and the thermal decomposition of their derivatives.

In the following pages, a review of the current position of indium chemistry is given with a particular emphasis placed upon those areas most relevant to the work carried out in this study. Further information on the areas not thoroughly covered can be found in two excellent reviews on indium chemistry, one on the co-ordination of indium trihalides by Carty and Tuck [2], and the other on the organometallic chemistry of indium.[3]

Group 13 Elements.

In general the chemistry of the group 13 elements (with the exception of thallium) is dominated by the stability of the +3 oxidation state. On descending the group, however, the +1 and to a lesser extent the +2 oxidation states become increasingly important. This is particularly true for thallium, for which the +1 oxidation state is very important, but also for indium for which the +1 and +2 oxidation states are known.

Compounds of the group 13 elements in the +3 oxidation state readily associate into dimers (or higher oligomers) or form complexes with electron donors in an effort to increase the number of electrons associated with that element.[4] A compound of a group 13 element with only three covalent bonds to it would have only six electrons associated with that element leaving it two short of a more stable "octet"

configuration. This makes such a compound electron deficient and is the driving force behind the subsequent formation of oligomers and co-ordination compounds that is common for compounds of group 13 elements. Thus, indium triiodide has been shown to be dimeric in the solid state with bridging iodides.[5] The structure of this dimer, as determined by an *X*-ray crystallographic study is shown in Diagram 1. In this case the donation of a pair of electrons from each of the two bridging iodides to the indium atoms leads to an In_2I_2 ring with four terminally bonded iodides.

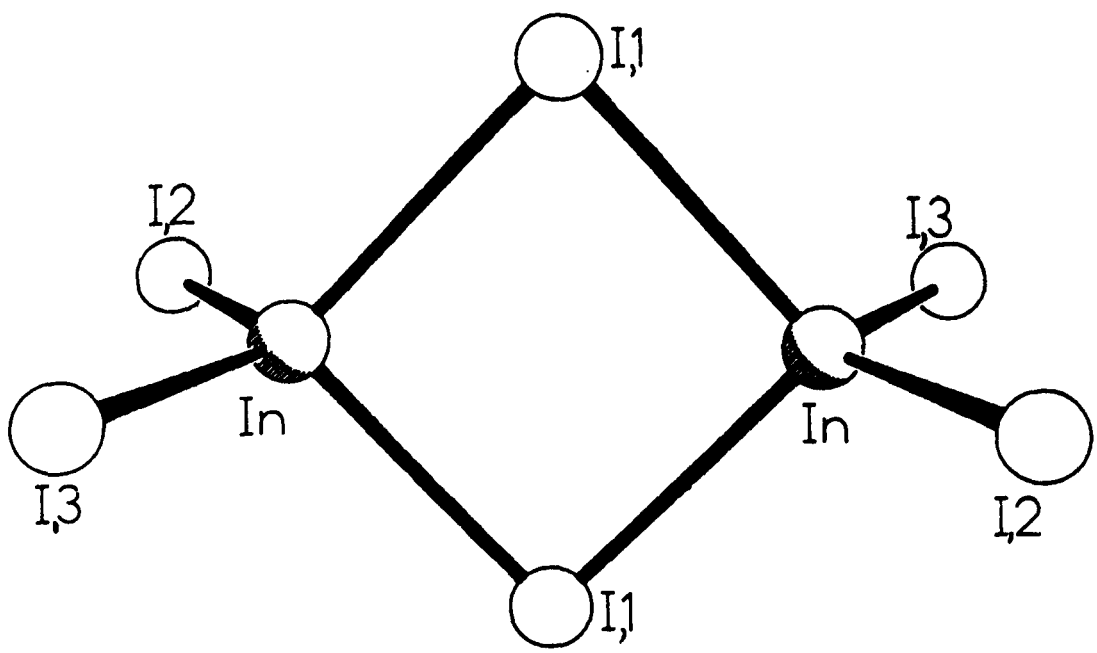


Diagram 1. View of the molecular structure of In_2I_6, showing the dimeric nature of the compound.[5]

In contrast to this indium trichloride and tribromide have been shown to be ionic in the solid state. Indium trichloride is isomorphous with aluminium trichloride.[6] That is it has the yttrium chloride structure with a distorted cubic close packed chloride ion lattice with one third of the octahedral holes filled. The structure of indium tribromide has not yet been conclusively determined. However, studies of its Raman spectrum have led to suggestion that it has an ionic lattice structure similar to that of indium trichloride.[7]

Comparisons of the chemistry of boron and aluminium with the heavier elements in the group shows several important differences. For boron a great many cluster compounds have been reported whereas for the other elements in the group such compounds are by comparison very rare indeed. The stability of the hydrido-compounds of these elements can also be seen to decrease on descending the group.[10]

A particularly important consideration to be taken into account when studying the co-ordination chemistry of the trihalides of the group 13 elements is the question of relative acceptor strengths. For the boron trihalides the answer to the question as to which compound will form the strongest donor-acceptor bonds is well established. The formation of 1:1 complexes between BX_3 (X=F,Cl,Br) and pyridine has been studied and the heats of formation of the complexes determined. These demonstrated that boron tribromide forms the strongest complexes and boron trifluoride forms the weakest complexes. That is, the relative acceptor strengths of the boron trihalides decrease in the order $BBr_3 > BCl_3 > BF_3$.[11] This order is the opposite to that which would be predicted from the electronegativities of the halides. The explanation for this, at least in part, is believed to lie in the π-bonding that is known to occur between the boron atom and the halides in the boron trihalides.

Electron density in the p-orbitals of the halides is thought to be donated to the vacant p_z orbital of the boron atom. This can be seen in Diagram 2.

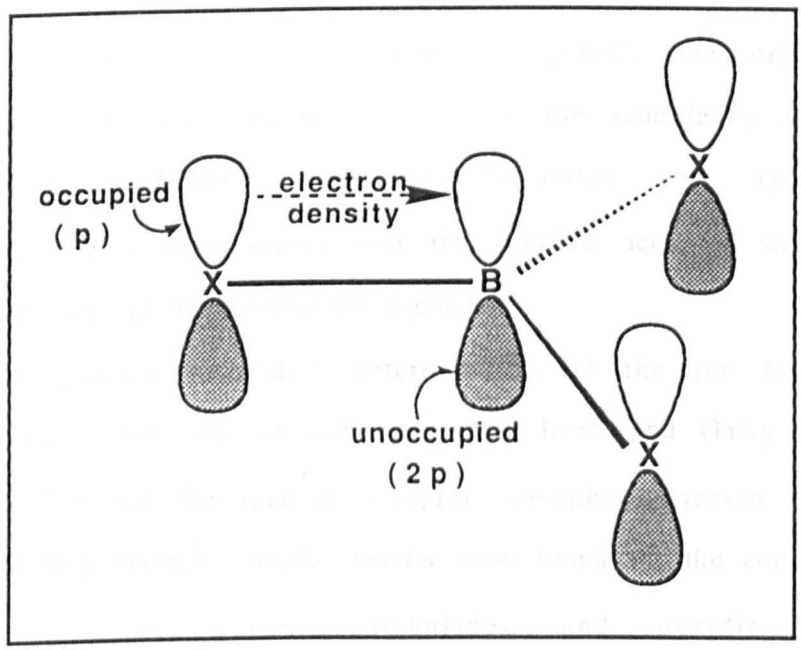


Diagram 2. Pictorial representation of the π-bonding in boron trihalides.

This form of π-bonding has been shown to be strong for all of the boron trihalides and to increase steadily in strength in the order $BI_3<BBr_3<BCl_3<BF_3$.[12] The change in strength of this π-bonding is most probably a result of the better orbital overlap that occurs between the orbitals of the lighter halides and the boron $2p_z$ orbital. For these boron trihalides to form complexes with a donor ligand, the increased energetic stability of the trigonal planar structure as a consequence of this π-bonding must be overcome. That is, to form a tetrahedral 1:1 complex the energetically favourable π-bonding must be largely destroyed. Clearly then, the stronger this π-bonding is, the less

favourable the formation of a complex is going to be. Hence the order of acceptor strengths observed for the boron trihalides.

On descending the group 13 elements, however, structural changes in the trihalides mean that the π-bonding found for boron trihalides is no longer significant, and consequently the order of relative acceptor strengths changes. Thus, for the complexes formed between AlX_3 (X=Cl,Br,I) and trimethylamine and pyridine, thermochemical studies have shown that the relative acceptor strengths of the trihalides are all approximately equal.[13]

For the gallium trihalides, determination of the the heats of formation of the complexes $GaX_3.Et_2O$, $GaX_3.Et_2S$ and $GaX_3.Me_2S$ (X=Cl,Br,I) showed that the relative acceptor strengths decreased in the order $GaCl_3>GaBr_3>GaI_3$.[14] Similar results were found for the complexes formed between the gallium trihalides and pyridine and triethylamine.[13]

For the indium trihalides, determinations of the heats of formation of 1:1 complexes formed with ethylacetate showed that $InCl_3$ was a stronger acceptor than $InBr_3$.[15] These determinations were also carried out on the ethylacetate complexes with trihalides of the other elements of group 13. This established that for the trichlorides, the relative acceptor strengths decreased in the order $BCl_3>AlCl_3>GaCl_3>InCl_3$. Studies of the pyridine complexes $InX_3.Py_3$ (X=Cl,Br,I) showed that although the heats of formation from the solid phase were all very similar, the probable heats of formation from the gas phase suggested that the relative acceptor strengths decreased in the order $InCl_3>InBr_3>InI_3$.[16]

Co-ordination Chemistry of the Indium Trihalides.

The co-ordination chemistry of the indium trihalides has previously been comprehensively reviewed by Carty and Tuck.[2] The following, is therefore an updated overview of the subject with emphasis placed upon the areas most relevant to the work carried out in this study.

Research on the co-ordination compounds of the indium trihalides has been concentrated on the chloride, bromide and iodide. A great variety of donor ligands has been used to prepare various complexes and as a general rule the indium in these has been found to be limited to a maximum co-ordination number of six.

Very little structural information on the solid state is available for these complexes. That which has been deduced (from Raman and infra-red spectra, and *X*-ray crystallography) shows that generalisations concerning the solid state structures cannot be readily made. It can, however, be said that the triiodide complexes have a greater tendency towards the formation of ionic species than the lighter halides. Thus an *X*-ray crystallographic study of the dimethylsulphoxide complex, $I_3In.(DMSO)_2$, has shown it to have an ionic dimeric structure, $[I_2In(DMSO)_4][InI_4]$.[17] In contrast to this, the indium trichloride and tribromide complexes with this ligand have the stoichiometry $InX_3.(DMSO)_3$. Interpretation of their infra red spectra suggests that they are monomeric and six co-ordinate neutral species.[18]

Very few studies have been carried out on solutions of indium trihalide-complexes. The results of those which have been reported are discussed in more detail in the following pages. However, in general these show that the solution chemistry of these compounds is

complicated. Most of the studies have been concentrated on molecular weight determinations and on conductivity measurements. For a few complexes it has been concluded that in solution the ligands are dissociated to a large degree and that in some cases dissociation into ionic species occurs.[19,20] Surprisingly, almost no n.m.r. studies have been carried out on these complexes in solution.

With monodentate ligands, the indium trihalides commonly form complexes with three stoichiometries, $X_3In.L$, $X_3In.L_2$ and $X_3In.L_3$.

Mono-Complexes of Indium Trihalides, ($X_3In.L$).

A comprehensive list of all of the 1:1 complexes known to form between the indium trihalides and monodentate ligands is given in Table 1. The majority of these are formed with indium triiodide. This is likely to be a result of the greater size of the iodides making the formation of a 1:1 complex sterically more favourable, as well as their greater polarisability leading to an effective reduction in charge on the metal and so also making the 1:1 complexes electronically more favourable.

No *X*-ray crystallographic studies have been reported for any of these 1:1 complexes. Consequently, the only structural information available is derived from studies of the vibrational spectra of these compounds. Such studies, however, have not been carried out for many of the known complexes and so the overall picture is somewhat limited.

The vibrational spectra of the complexes formed with some of the nitrogen and oxygen donor ligands in Table 1 (pyridine, 2,6-lutidine, α-picoline, β-picoline, 2,6-lutidine-N-oxide and 2-picoline-N-oxide) have

Table 1. Mono-Complexes of Indium Trihalides.

Ligand	Halide	Reference
Ammonia	Cl,I	21
Pyridine	Br,I	22
Trimethylamine	I	16
Diphenyl(vinyl)phosphine	I	23
Triphenylphosphine	I	20
Tri-*p*-tolylphosphine	I	24
Tri-*p*-methoxyphenyl-phosphine	Br,I	24
Tricyclohexylphosphine	Cl,Br,I	19
Phosphorylchloride	Cl	25
1,4-Dioxane	I	26
Diethylether	I	26
Di-*n*-butylether	I	26
Di-*n*-propylether	I	26
Tetrahydrofuran	Cl	26
Ethylacetate	Cl,Br	27
Acetone	Cl	28
Benzophenone	Cl	28
α-Picoline	I	22
β-Picoline	Br,I	22
2,6-Lutidine	Br,I	22
2,6-Lutidine-*N*-oxide	Br,I	22
2-Picoline-*N*-oxide	I	22
Diethylsulphide	I	29
$Me_2NC_6H_4R$ (R=CHO,Me,H)	Cl	2

been reported.[22] None of these, however, gave rise to a conclusive assignment of a solid state structure. For a four co-ordinate monomer with C_{3v} geometry around the indium, group theory predicts six bands corresponding to metal-ligand modes.[30] For the above complexes studied, however, more than six bands were observed in each case. This could indicate that the symmetry is lower than C_{3v} (hence more than six bands), or for the heavier halides (Br,I) it could be a result of coupling between the indium-halide stretching modes with the indium-ligand rocking modes giving rise to a more complicated spectrum.[22]

Only one 1:1 complex with a sulphur donor ligand ($InI_3.SEt_2$) has so far been reported. This may be due simply to a lack of research in this area rather than to any chemical reason. No structural information of any kind was reported for this complex.[29]

Bis-Complexes of Indium Trihalides, ($X_3In.L_2$).

A comprehensive list of all of the 1:2 complexes known to form between the indium trihalides and monodentate ligands is given in Table 2. Four of these 1:2 complexes have had their structures determined by a complete single crystal *X*-ray diffraction study. Three of these (L= triphenylphosphine [38], trimethyl-amine [39] and hexamethylphosphoramide [37]) were all found to have the same trigonal bipyramidal geometry around the indium. The structure of the trimethylamine adduct is shown as an example in Diagram 3. As is the case for all three structures the ligands occupy the *trans*-axial positions with the three chlorides in the equatorial positions.[39]

Table 2. Bis-Complexes of Indium Trihalides.

Ligand	Halide	Reference
Ammonia	Cl,I	21
Pyridine	Cl,Br	22
α-Picoline	Br	22
β-Picoline	Cl,Br	22
2,6-Lutidine	Cl	22
Imidazole	Cl,Br,I	31
Tetrahydro-benzimidazole	Cl,Br,I	31
Pyrazoles	Cl,Br,I	31
Benzazoles	Cl,Br,I	31
Trimethylamine	Cl,Br,I	32
Acetonitrile	Cl,I	33,34
Triphenylphosphine	Cl,Br,I	20
Tri-*p*-tolylphosphine	Cl,Br	24
Tri-*p*-methoxyphenyl-phosphine	Cl	24
Dimethylphenylphosphine	Cl,Br,I	19
Diphenylmethylphosphine	Cl	23
Diphenylethylphosphine	Cl,Br	19
Diphenyl-*p*-tolyl-phosphine	Cl	23
Trimethylphosphine	Cl,Br,I	19
Triethylphosphine	Cl,Br,I	19
Tricyclohexylphosphine	Br	18
$Ph_2PCH_2CH_2CH{=}CH_2$	I	23
Dimethylsulphoxide	I	20
Triphenylphosphineoxide	I	20
Trimethylamine-*N*-oxide	Cl	35
2,6-Lutidine-*N*-oxide	Cl	22
1,4-Dioxane	Cl,Br,I	26
Di-*n*-propylether	I	26
Di-*n*-butylether	Br,I	26

Table 2. (Cont'd).

Ligand	Halide	Reference
Diethylether	Cl,Br	26
Dimethylether	Cl,Br,I	26
Tetrahydrofuran	Cl,Br	26
2-Methyltetrahydrofuran	Cl	26
2,5-Dimethyltetra-hydrofuran	Cl	26
Dimethylsulphide	Cl,Br,I	29
Diethylsulphide	Cl,Br,I	29
Tetrahydrothiophen	Cl,Br,I	29
4-Cyanopyridine	Cl	36
Hexamethyl-phosphoramide	Cl	37

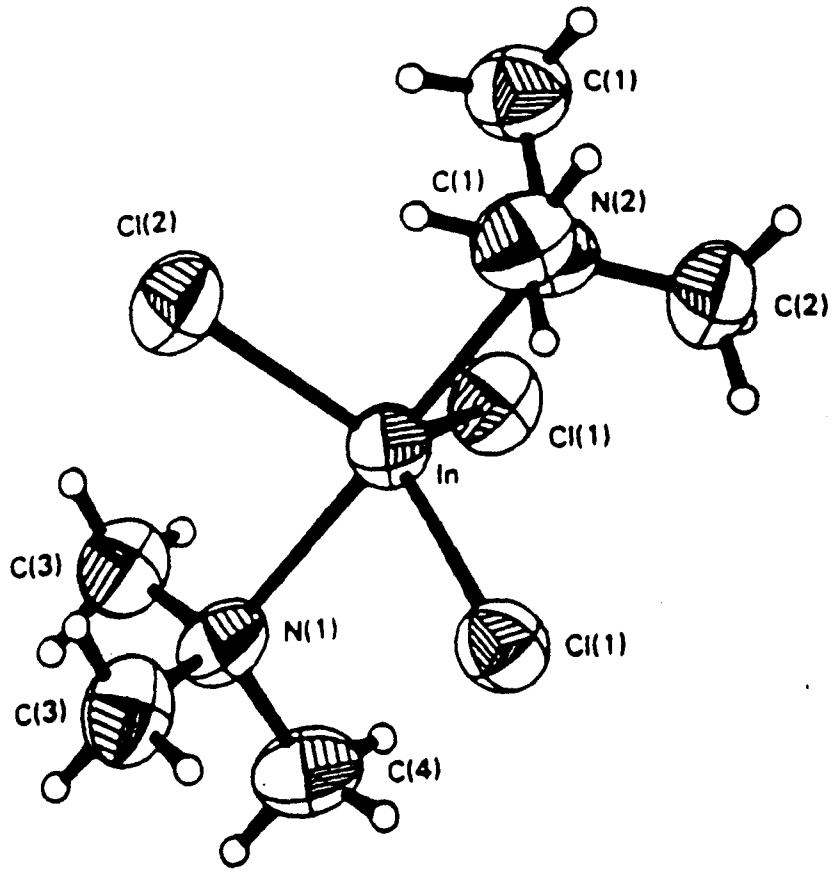


Diagram 3. Molecular structure of $InCl_3(NMe_3)_2$. Thermal ellipsoids are drawn at the 50% probability level.[39]

The fourth structure that has been determined crystallographically is that for the dimethylsulphoxide complex with indium trichloride. This was found to have a different structure to those mentioned above and is an ionic dimer of formulation $[I_2In(DMSO)_4][InI_4]$. The anion was found to have a tetrahedral geometry around the indium and the cation was found to have an octahedral geometry around the indium with a *cis*-arrangement of the iodides.[17]

Further structural information on the 1:2 complexes has been obtained from studies of their vibrational spectra. The infra-red spectrum of the trimethylamine complex in the solid state has been reported [32] and as the structure of this complex is known, the data has been used to help assign structures for other complexes with nitrogen donor ligands. Comparisons of the infra-red spectra of the complexes formed between indium trichloride and 2,6-lutidine, pyridine and β-picoline led to the conclusion that these too are isostructural with the trimethylamine complex and have D_{3h} symmetry around the indium.[22]

The vibrational spectra of the 1:2 complex formed between acetonitrile and indium triiodide have been shown to indicate the presence of the $[InI_4]^-$ anion and so it was concluded that this complex has a similar structure to the dimethylsulphoxide complex already described, namely $[I_2In(MeCN)_4][InI_4]$.[34]

The vibrational spectra of the complexes with phosphines listed in Table 2 (trimethlyphosphine, dimethyl(phenyl)phosphine, diphenyl(ethyl)-phosphine and triethylphosphine)[19] have been interpreted as showing in the case of the chlorides and bromides that they all have D_{3h} symmetry with a trigonal bipyramidal structure as found crystallographically for the triphenylphosphine complex.[38] The indium triiodide complexes with these phosphines appear to be significantly different from those for the trichloride and tribromide derivatives. The vibrational spectra for these complexes were found to be too complicated to assign D_{3h} symmetry.[19] The situation has yet to be resolved.

In general, two types of solid state structures have been found for the 1:2 complexes. One based upon a trigonal bipyramidal geometry and the other based upon an ionic dimer. However, too few structures have

been conclusively assigned for predictions of which complex will have which structure to be made, although to date, only indium triiodide complexes have been shown to have the ionic structure.

Solution studies (conductivity measurements) on complexes of three ligands (pyridine, triphenylphosphine oxide and triphenylphosphine) have shown that with all of the indium trihalides substantial ionisation (up to 50%) occurs in nitromethane solutions (10^{-3} mol dm^{-3}). The degree of ionisation was found to decrease with increasing concentration.[20]

Tris-Complexes of the Indium Trihalides, $X_3In.L_3$.

A comprehensive list of all of the 1:3 complexes known to form between the indium trihalides and monodentate ligands is given in Table 3.

No *X*-ray crystallographic studies have been reported for any of these complexes, however, the 1:4 complex formed with pyridine, $InCl_3.Py_4$, has had its structure determined and was found to have only three of the pyridine molecules directly bonded to the indium (the fourth was unco-ordinated in the lattice). The six indium bonded atoms (3Cl,3N) in this complex are arranged with an approximate octahedral geometry around the indium with the three pyridines having a *mer*-configuration. The structure of the complex is shown in Diagram 4.[44] The same structure was also found crystallographically for the analogous complex with indium tribromide.[45] As for the 1:1 and 1:2 complexes, further information on these 1:3 complexes has been obtained from studies of their vibrational spectra. The infra-red spectrum of the 1:3 pyridine complex $InCl_3.Py_3$ was interpreted as

Table 3. Tris Complexes of Indium Trihalides.

Ligand	Halide	Reference
Ammonia	F,Cl,Br,I	21
Pyridine	Cl,Br,I	2
α-Picoline	Cl,Br,I	22
β-Picoline	Cl,Br,I	22
γ-Picoline	Cl,Br,I	22
4-Cyanopyridine	Cl	36
n-Propylamine	Cl,Br,I	2
Diethylamine	Cl	2
Aniline	Cl	2
Quinoline	Cl	2
β-Napthylamine	Cl	2
Benzidine	Cl	2
Dimethylphenylphosphine	Cl,Br	19
Urea	Cl,Br,I	20
Dimethylsulphoxide	Cl,Br	20
Diphenylsulphoxide	Cl	40
Pyridine-*N*-oxide	Cl,Br,I	22
4-Picoline-*N*-oxide	Cl,Br,I	22
1,4-Dioxane	I	26
N,N-Dimethyformamide	Cl,Br	41
Tetramethylene-sulphoxide	Cl	42
Acetonitrile	Cl	43
Dimethylsulphide	I	29

showing that there is an octahedral geometry around the indium. Surprisingly, it was concluded that the three pyridines had a *fac*-geometry and not the *mer*-geometry that might have been expected by comparison with the structure of the 1:4 complex discussed above. The infra-red spectrum of the dimethylsulphoxide complex has been reported and this was shown to be consistent with an octahedral geometry around the indium with the ligands in the *mer*-configuration.[18]

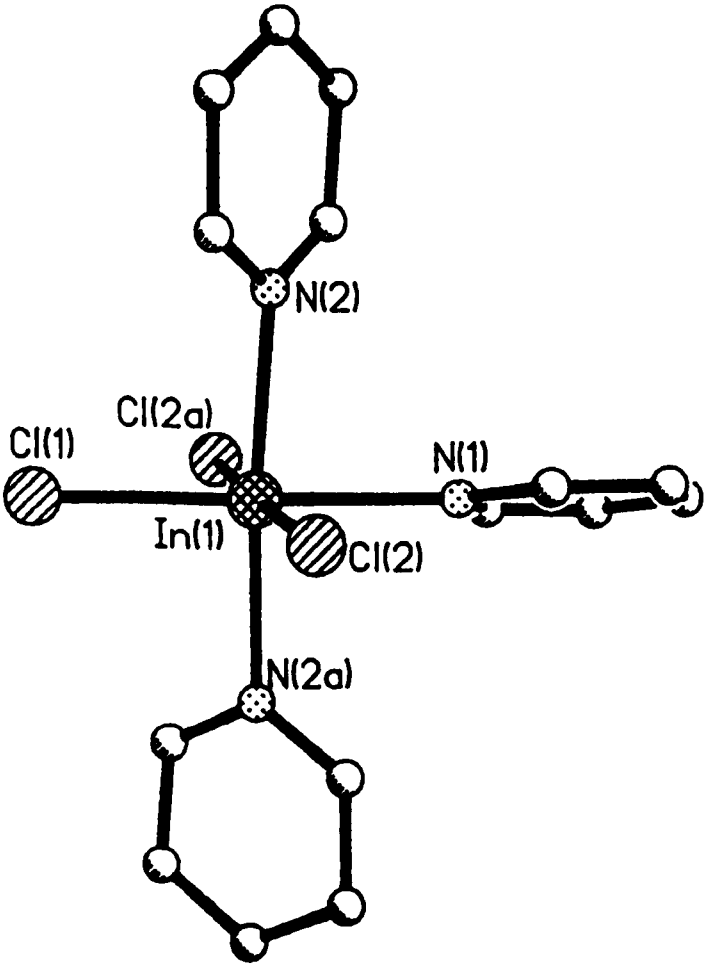


Diagram 4. Molecular structure of $Cl_3In.Py_4$ showing the *mer*-geometry of the octahedral metal complex.[44]

The 1:3 complexes with 4-cyanopyridine[36], pyridine [22] and dimethylsulphide [29] have been shown to be very labile with respect to the loss of ligands. The pyridine and dimethylsulphide complexes lose ligands on heating, whereas the 4-cyanopyridine complex dissociates simply on washing with acetone.

$InI_3(Et_2S)_3 \xrightarrow{\Delta} InI_3(Et_2S)_2$

$InCl_3.Py_3 \xrightarrow{160°C} InCl_3.Py_2 \xrightarrow{\Delta} Dec.$

$InBr_3.Py_3 \xrightarrow{160°C} InBr_3.Py_2 \xrightarrow{200°C} InBr_3.Py \xrightarrow{\Delta} Dec.$

$InI_3.Py_3 \xrightarrow{180°C} InI_3.Py \xrightarrow{\Delta} Dec.$

$InCl_3(PyCN)_3 \xrightarrow{Acetone} InCl_3(PyCN)_2$

Unusual Indium Trihalide Complexes.

At first sight some indium trihalide complexes with monodentate ligands appear to have a co-ordination number greater than six. On closer examination, however, the indium in these complexes is usually found to be six co-ordinate. For example, the 1:4 pyridine complex already described has an unco-ordinated ligand held in the lattice.[44]

A structurally unusual complex is formed between trimethylarsine oxide and indium trichloride, $(InCl_3)_2(Me_3AsO)_3$. An *X*-ray crystallographic study of this compound showed that the ligands are co-ordinated through the oxygen atoms and are bridging between two indium atoms. This gives rise to a distorted octahedral geometry around each indium (six co-ordination). There is also a C_3 symmetry axis

running through the two indium centres. The structure is shown in Diagram 5.[46]

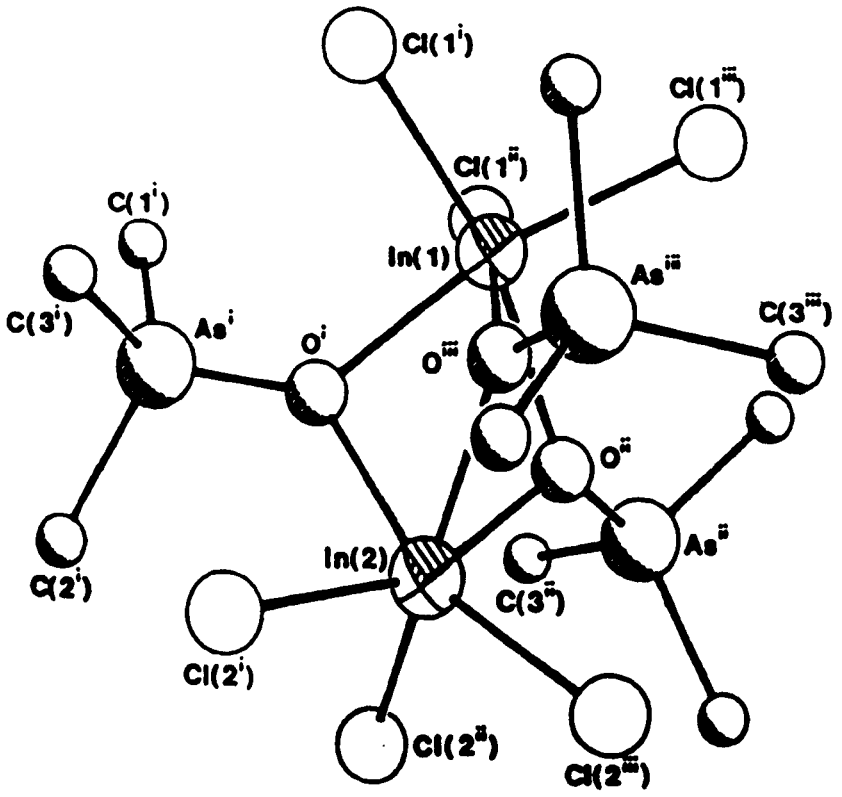


Diagram 5. Molecular structure of $(InCl_3)_2(Me_3AsO)_3$.[46]

A further class of complexes of interest is that with multidentate ligands. Complexes of indium trichloride with bidentate ligands such as 1,10-phenanthroline and 2,2'-bipyridyl have been prepared with a stoichiometry of 1:1.5, $Cl_3In.L_{1.5}$. Studies on their far infra-red spectra have led to them being assigned an ionic structure written as $[Cl_2InL_2][InCl_4L]$.[47] Further evidence for this ionic structure was obtained by the separate isolation of the two constituent ions from a solution of the 2,2'-bipyridyl complex. Thus reaction of this complex

with potassium hexafluorophosphate precipitated $[In(bipy)_2Cl_2]PF_6.H_2O$, while reaction with tetraphenylarsonium chloride precipitated $[AsPh_4][InCl_4.bipy].MeCN$.[47] Bis-1,2-diphenylphosphinoethane (diphos) complexes have also been prepared with 1:1 stoichiometries ($InX_3.L$; X=Br,I). For these, however, no structural information was reported.[20]

In conclusion then, it can be said that some important and intriguing questions on both the structural aspects and stoichiometries of complexes of the indium trihalides require to be answered, and it is also apparent that the complexes of indium triiodide have received less attention than those of indium tribromide and trichloride. Only one *X*-ray crystallographic study has been carried out on an indium triiodide complex and comparatively few conclusive studies of vibrational spectra have been reported. For this reason it was decided to concentrate the work in this study on the co-ordination chemistry of indium triiodide and for reasons mentioned earlier, to concentrate specifically on the co-ordination chemistry with phosphine ligands. Finally a relevant point with respect to synthetic studies involving the indium trihalides, is that of all the trihalides it is the triiodide which is the most convenient to prepare. In the present work, as described later, the preparation of the tiiodide from the elements has been improved to the point that this material is now available in a pure form and in large quantities.

Phosphine Complexes of Indium Triiodide.

Indium triiodide will form both 1:1 and 1:2 complexes with a variety of phosphine ligands. All of the known complexes are given in Table 4. As for indium trihalide complexes in general, information

Table 4. Phosphine Complexes of Indium Triiodide.

Ligand (L)	Complex	Ref.
PPh_3	$InI_3.L_2$	20
	$InI_3.L$	20
$P(p\text{-}CH_3C_6H_4)_3$	$InI_3.L$	24
$P(p\text{-}CH_3OC_6H_4)_3$	$InI_3.L$	24
$P(Me)_2Ph$	$InI_3.L_2$	20
PMe_3	$InI_3.L_2$	20
PEt_3	$InI_3.L_2$	20
$P(C_6H_{11})_3$	$InI_3.L$	20
$P(CH{=}CH_2)Ph_2$	$InI_3.L$	23
$P(CH_2CH_2CH{=}CH_2)Ph_2$	$InI_3.L_2$	23
$Ph_2CH_2CH_2PPh_2$	$InI_3.L$	20

concerning the solid state and solution behaviour for these complexes is very limited. Those studies that have been carried out are discussed below.

Solid State Structures.

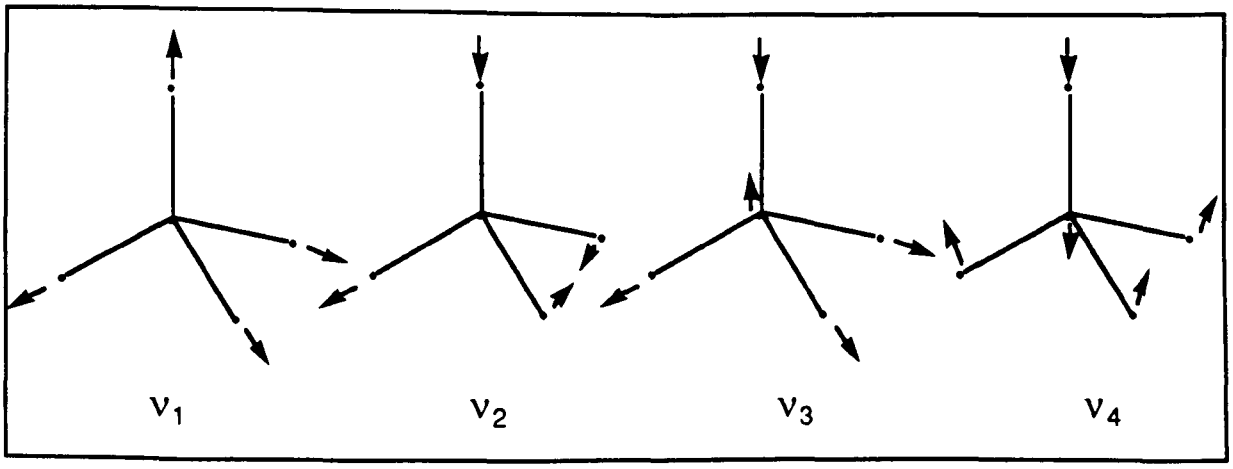
No *X*-ray crystallographic studies have been carried out on any of the indium triiodide-phosphine complexes that have been reported. In fact, only one crystal structure has been reported on any indium triiodide complex, the dimethylsulphoxide adduct (DMSO) which has already been described and was shown to be ionic.[17] The only indium trihalide-phosphine complex to have had its structure determined by a single crystal *X*-ray diffraction study is the triphenylphosphine adduct, $InCl_3.(PPh_3)_2$, which was shown to have a trigonal-bipyramidal geometry around the indium.[38]

The experimental tool which has been most commonly used in the deduction of solid state structures for these complexes is vibrational spectroscopy. Both Raman and infra-red spectroscopy have been used to study the indium-iodide and indium-ligand stretching frequencies. These bands, however, are usually found below 200 cm^{-1}, which is not a region of the spectrum that is routinely available on infra-red spectrometers in common use.

Raman Spectroscopy.

The Raman spectrum of the anion $[InI_4]^-$ has long been known.[48] For a tetrahedral species such as this (T_d symmetry), four In-I vibrational frequencies are expected. For this anion these have been

shown to occur at 42 (ν_2), 58 (ν_4), 139 (ν_1) and 185 cm^{-1} (ν_3). These are shown diagrammatically below.[30]



Replacement of one of the iodides with a different ligand lowers the symmetry to C_{3v} and consequently six vibrational frequencies are expected.[30] In practice, the quality of the spectra, intensity of the bands and possible further lowering of the molecular symmetry through intermolecular interactions (as discussed in Chapter 2) makes assignment of each band difficult.

Several indium triiodide-phosphine complexes have been studied using Raman spectroscopy. Some of these spectra and those for In_2I_6 and the $[InI_4]^-$ anion are summarised in Table 5. It has been shown for phosphine complexes of indium triiodide that all of the metal-ligand stretching modes are found below 400 cm^{-1} and so only the bands observed in this range are given. Raman spectroscopy has been used to differentiate between ionic type structures which contain the $[InI_4]^-$ anion (such as is found for $I_3In.(DMSO)_2$) and the monomeric tetrahedral alternative. The Raman spectrum of $I_3In.(DMSO)_2$ shows a strong band at 141 cm^{-1} and a weaker band at 183 cm^{-1} which have

Table 5. Raman Data (below 400 cm^{-1}) of indium-iodine compounds (all bands are in cm^{-1}).

$[InI_4]^-$ ref. (48)	In_2I_6 (49)	$InI_3.(Me_2PPh)_2$ (19)	$InI_3.(PMe_3)_2$ (50)	$InI_3.(PEt_3)_2$ (19)	$InI_3.PCy_3$ (19)	$InI_3.(DMSO)_2$ (51)
42(w)	40(w)					
	45(w)					
58(w)	52(w)					
	64(w)					
	76(w)		75(w)			
			79(w)			
			90(w)			
			98(w)			
	120(w)		120(w)	123(w)		
		130(w)				
139(vs)	**135(s)**	**141(vs)**		**140(vs)**	**138(vs)**	**141(vs)**
		145(w)				
			151(vs)			
				165(w)	162(w)	
		165(w)				
				176(w)		
185(m)	**185(m)**		190(w)	181(w)	185(w)	183(w)
					191(w)	192(w)
	220(w)			191(w)	198(w)	198(w)
					220(w)	
		261(w)	260(w)			
				311(w)		310(w)
		306(w)	318(w)		320(w)	
		324(w)		336(w)		
						344(w)
				369(w)		

*This region contains the normal In-I and In-P stretching modes. It can be seen that the complexity of this region makes definite assignments of bands in many cases impossible.

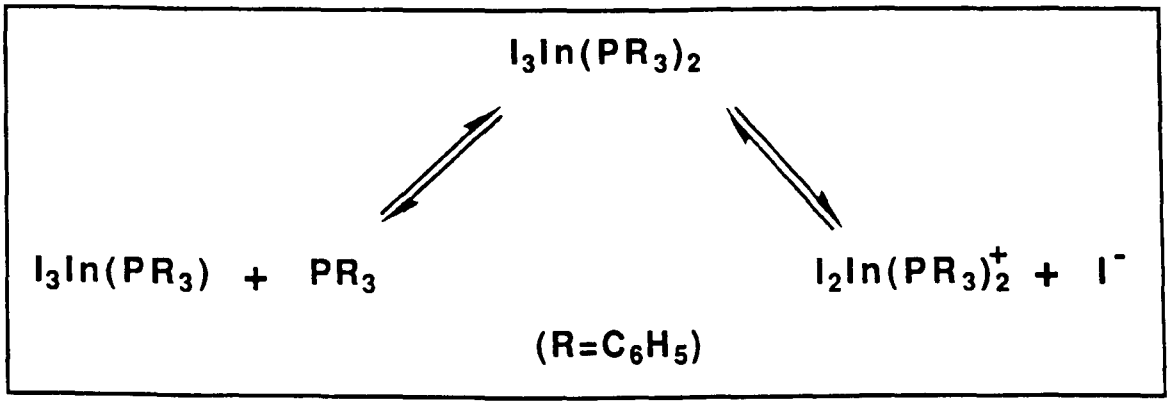
been assigned as the ν_1 and ν_3 stretching modes of the $[InI_4]^-$ anion respectively.[51] Similarly the bands in the Raman spectrum of $I_3In.PCy_3$ at 138 and 185 cm^{-1} have led to suggestions that this complex is also ionic and contains the $[InI_4]^-$anion. The ionic structure proposed for this complex can be written as $[I_2In(PCy_3)_2][InI_4]$.[19] The spectrum of this complex, however, is complicated and shows five bands in the In-I region of the spectrum (100-200 cm^{-1}) and so the assignment of this structure cannot be unambiguous. A further complication to be considered is that the In-P modes are also found in this region of the spectrum. For the complex $InCl_3(PMe_3)_2$ the P-In-P stretching mode has been shown to give rise to a band at 135 cm^{-1} in the Raman spectrum.[52] The Raman spectra of the indium trichloride and tribromide complexes with tricyclohexylphosphine are, in comparison to the spectrum for the triiodide complex, relatively simple. These show only two strong bands that can be assigned as In-X stretching modes. It was concluded from this that these complexes are tetrahedral monomers.[19]

Solution Behaviour.

Most of the solution studies that have been carried out on indium triiodide systems have been concentrated on conductivity measurements and molecular weight determinations. The triphenylphosphine complex, $I_3In.(PPh_3)_2$, has been studied in some detail.[20] Molar conductivity measurements on nitrobenzene solutions for a range of concentrations have shown that this complex is a weak electrolyte in this solvent. Molecular weight determinations for this complex gave values of 526 in benzene and 614 in chloroform. These differ

significantly from the expected value of 1020 and show that the complex is highly dissociated in these solutions.

These studies led to proposals that in solution several solvent dependent equilibria were occurring, involving either dissociation of the phosphine ligands or of the iodides.[20] These equilibria are summarised below.



The 1:1 indium triiodide complexes with phosphines which have previously been reported together with the proposals made regarding their structures are summarised in Table 6. The complexes formed with tri-*p*-tolyl- and tri-*p*-methoxyphenyl-phosphine have been subjected to conductivity measurements which showed that they were almost completely ionised into a 1:1 electrolyte in nitrobenzene solution. It was suggested that they have an ionic type structure of formulation $[I_2In(PR_3)_2][InI_4]$.[24] This is similar to the solid state structure which was proposed for the tricyclohexyl phosphine complex on the basis of its Raman spectrum.[19]

Table 6. 1:1 Phosphine complexes of indium triiodide.

Phosphine	Structure	Reference
PPh_3	Covalent monomer[b]	20
PCy_3	Ionic dimer[b]	19
$P(p\text{-}Tol)_3$	Ionic dimer[a]	24
$Ph_2P(CH{=}CH_2)$	Covalent monomer[b]	23
$P(p\text{-}MeOC_6H_4)_3$	Ionic dimer[a]	24

(a) Based upon conductivity measurements in nitrobenzene.
(b) Based upon vibrational spectroscopy in the solid state.

N.m.r. Studies.

Surprisingly little use has been made of n.m.r. spectroscopy in the study of indium trihalide complexes with phosphines. The ^{1}H-n.m.r. spectra of a series of phosphine complexes have been reported.[19] For the 1:2 complexes formed with dimethyl(phenyl)phosphine, $X_3In(Me_2PPh)_2$, the signal corresponding to the methyl groups was found to be a 1:1 doublet. For transition metal complexes with phosphines in *trans* positions it has been shown that this methyl signal is a 1:2:1 triplet arising from coupling with both of the phosphines (virtual coupling) whereas in *cis* positions a 1:1 doublet is observed.[53] It is not known whether this phenomenon can generally be applied to main group metals but it was concluded that the absence of virtual coupling does not necessarily show that the 1:2 complexes of indium triiodide have a *cis* arrangement of the ligands. Rapid exchange of the

phosphine ligands in solution would also lead to a doublet as the two phosphines would be rendered equivalent on the n.m.r. time scale.[19]

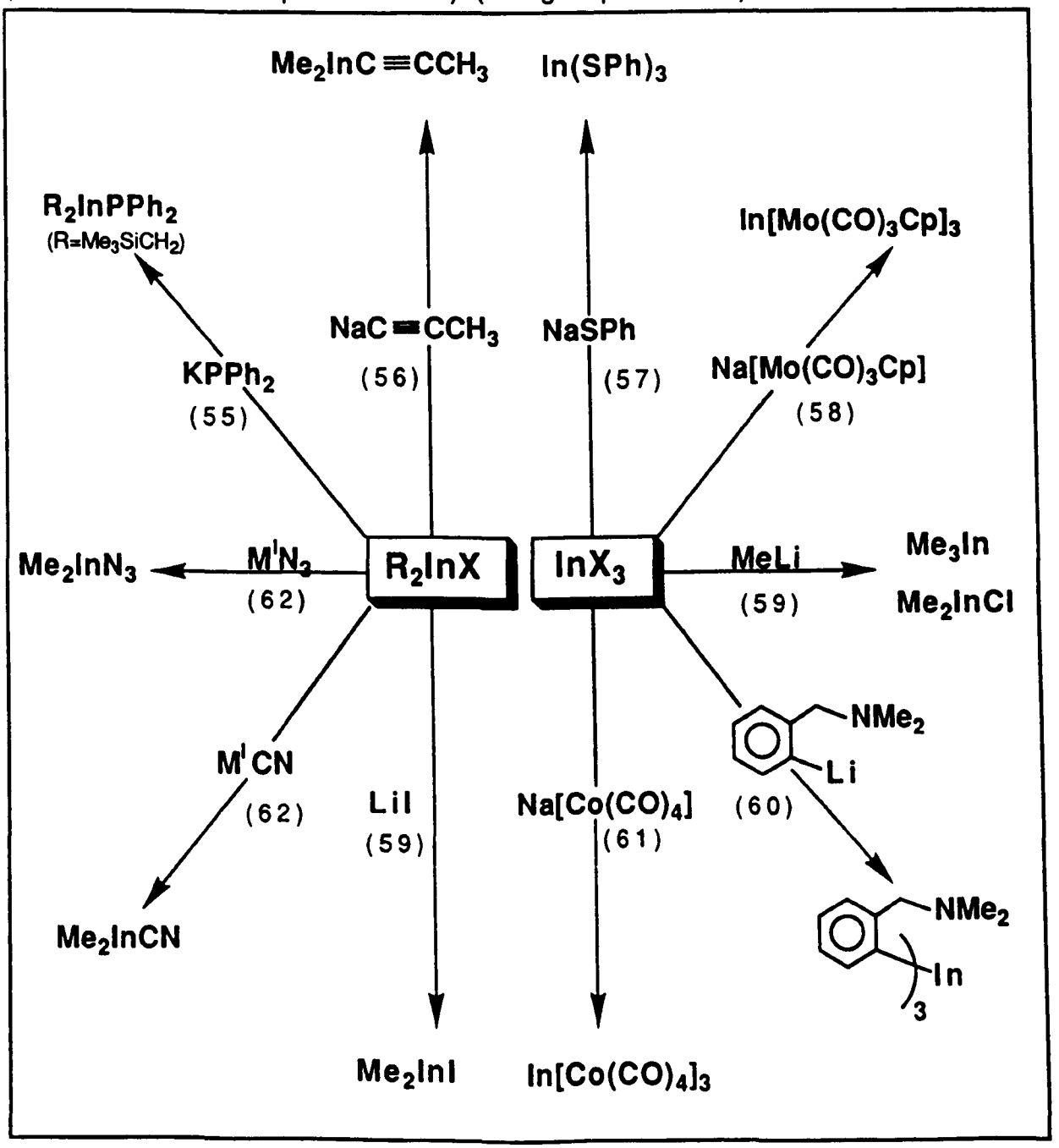
The n.m.r. spectra of other nuclei have been employed to an even lesser extent. Some ^{115}In-n.m.r. studies have been reported.[54] This quadrupolar nucleus gives signals that are extremely broad. For most species the signals are so broad that they cannot be observed. However, for highly symmetrical species (tetrahedral or octahedral) in which all of the ligands are identical (for example $[In(H_2O)_6]^{3+}$ and $[InX_4]^-$)[8,9] the signals are sharper and can be observed (half-height line widths of 1000 Hz or less for $[InX_4]^-$ anions). This offers an excellent method for identifying the presence of the tetrahedral $[InI_4]^-$ anion in solution.[54] No other significant n.m.r. studies on other nuclei have been carried out on the phosphine complexes. This is particularly surprising in view of the potential applications of ^{31}P-n.m.r. spectroscopy to this area of chemistry.

Metathetical Reactions of Indium Halides.

The indium trihalides and the dialkylindium halides have been shown to undergo a great many different metathetical reactions with group 1 metal derivatives. In each case these proceed with the elimination of the corresponding group 1 metal halide and the formation of the new indium derivative, usually in high yield. Diagram 6 shows some of the reactions of this type that have been reported. This is not by any means comprehensive, but is meant only to give a feel for the variety of these reactions that are known.

The metathetical reaction that has been put to most use is the reaction between indium trichloride and methyllithium. It has been

Diagram 6. Metathetical Reactions of Indium Halides.
(References are in parentheses) (M^1=group 1 metal)



shown that three equivalents of methyllithium will react with one equivalent of indium trichloride in diethylether at room temperature to give an almost quantitative yield of trimethylindium.[59]

$$3MeLi + InCl_3 \xrightarrow{Et_2O} InMe_3 + 3LiCl$$

It was also shown that dimethylindium chloride can also be prepared by this method under the same conditions by using only two equivalents of methyllithium. The only difference is that for this compound the reaction takes approximately two days instead of the thirty minutes that were required to prepare trimethylindium. It was demonstrated that if the preparation of dimethylindium chloride was stopped after thirty minutes then the reaction mixture contained trimethylindium and indium trichloride only. Presumably then the initial product in this reaction is trimethylindium, which then undergoes a ligand redistribution reaction with the remaining indium trichloride to give dimethylindium chloride.[59]

$$2MeLi + InCl_3 \xrightarrow{Quickly} 2/3InMe_3 + 1/3InCl_3 + 2LiCl$$

$$2/3InMe_3 + 1/3InCl_3 \xrightarrow{Slowly} Me_2InCl$$

These reactions involving indium trichloride are the only reactions that have been reported between methyllithium and the indium trihalides; the corresponding reactions with indium tribromide or triiodide have not yet been reported.

One of the reactions in Diagram 6 is of particular interest so far as the preparation of precursors for indium phosphide is concerned. Potassium diphenylphosphide has been shown to react with $(Me_3SiCH_2)_2InBr$ to give the corresponding (diphenylphosphido)indium compound, $[((Me_3SiCH_2)_2InPPh_2)_2]$. The reaction was found to proceed in high yield in diethylether solution with the elimination of potassium bromide.[55]

$$(Me_3SiCH_2)_2InBr + KPPh_2 \longrightarrow 1/2[(Me_3SiCH_2)_2InPPh_2]_2 + KBr$$

The product of this reaction was shown by *X*-ray crystallography to be dimeric with an In_2P_2 ring. (This is discussed in more detail later (page 55) and the structure is shown in Diagram 11 (page 56).

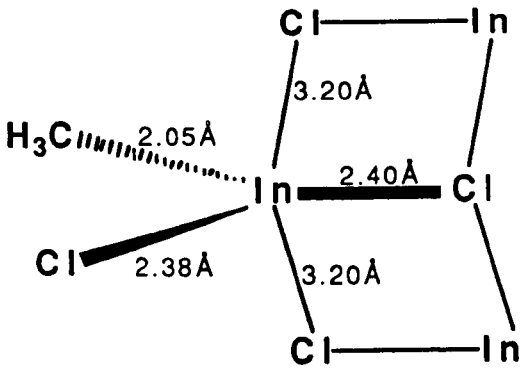
Organometallic Derivatives of Indium.

A great variety of trialkyl and triaryl indium compounds have been prepared. The mixed alkyl-halide compounds ($RInX_2$ and R_2InX) are also well established. Most of the work that has been carried out on these compounds has been concentrated on the methyl, ethyl and phenyl derivatives.[3]

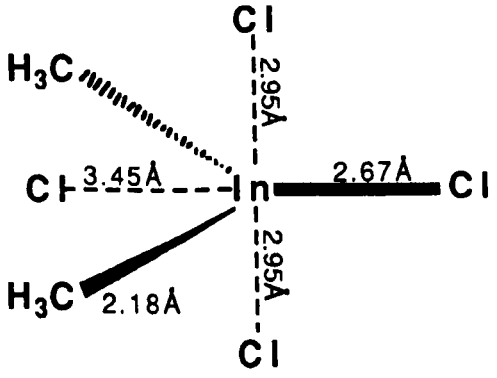
Organoindium Halides.

Although some organoindium fluorides have been reported (Me_2InF [59] and Et_2InF[78]) very little is known about them. NQR studies

have been interpreted as showing that the indium in these compounds is five co-ordinate, however, no other information is available.[64] Much more information is available for the other organoindium halides. Me_2InCl and $MeInCl_2$ have both had their structures determined by *X*-ray crystallography. The structure of $MeInCl_2$ shows planar molecules which are stacked on top of each other in such a way that the indium atoms attain a distorted trigonal bipyramidal environment consisting of four chlorine atoms and one carbon atom. This is shown below.[65]



Me_2InCl has been shown to have a similar planar structure but with the molecular units packed in such a manner that the indium atoms attain six co-ordination at the centre of a highly distorted octahedron consisting of four chlorine atoms and two carbon atoms [66] :-



Me_2InBr has been shown to be ionic in the solid state with linear $[Me_2In]^+$ cations. In the structure each indium atom is additionally surrounded by four bromide ions and so attains an approximate tetragonal bipyramidal environment.[67] The structure of $MeInBr_2$ has not been determined by *X*-ray crystallography, but NQR studies on this compound have, however, been interpreted as showing that it is a bromide bridged dimer.[64] NQR and Raman studies have also indicated that $MeInI_2$ has an ionic structure of formulation $[Me_2In][InI_4]$, and that $EtInI_2$ has a dimeric structure with two bridging iodides.[64,68] The structure of dimethylindium iodide has not yet been determined, although NQR studies have shown that the C-In-C unit is linear indicating the possible presence of the $[Me_2In]^+$ cation.[64]

Co-ordination Chemistry of Organoindium Halides.

All of the known co-ordination compounds of the organoindium halides are listed in Table 7. Only two of the complexes listed have had their structures determined by *X*-ray crystallographic studies. The *t*-butylamine complex, $MeInCl_2(H_2NBu^t)$, was found to be polymeric with N-H····Cl linkages between the molecules. The indium atoms were found to have a distorted tetrahedral environment with a Cl-In-Cl bond angle of 100.5(1)°.[73]

The TMEDA complex, $EtInI_2$(TMEDA), was found to be monomeric. The indium atom in the molecule is five co-ordinate and has a quasi-trigonal bipyramidal environment. The structure that was determined is shown in Diagram 7.[71]

Table 7. Co-ordination Compounds of the Organoindium Halides.

Ligand(L)	Complex	Halide	Ref.
Pyridine	$MeInX_2.L_2$	Cl	69
	$Me_2InX.L$	Cl,I	59
Triphenylphosphine	$(Me_2InX)_2L$	Cl	59
	$Me_2InX.L$	I	59
Triphenyl-phosphineoxide	$Me_2InX.L$	Cl,I	69
Triphenyl-arsineoxide	$Me_2InX.L$	Cl	69
*Ammonia	$Me_2InX.L$	Cl,I	69
	$MeInX_2.L_2$	Cl,I	69
	$MeInX_2.L_3$	Cl,I	69
1,2-Diaminoethane	$Me_2InX.L$	Cl,I	69
1,10-Phenanthroline	$Me_2InX.L$	Cl	69
	$Cp_2InX.L$	I	70
TMEDA	$EtInX_2.L$	I	71
2,2'-Bipyridyl	$Me_2InX.L$	Cl,I	69
	$Et_2InX.L$	I	72
	$MeInX_2.L$	I	72
	$EtInX_2.L$	Br	72
	$PhInX_2.L$	Cl,Br,I	72
	$CpInX_2.L$	I	70
	$BzInX_2.L$	Cl,Br,I	72
	$C_6F_5InX_2.L$	Br	72
t-Butylamine	$MeInX_2.L$	Cl	73
1,4-Dioxane	$BzInX_2.L$	Br,I	74
	$(Allyl)InX_2.L$	Br,I	74
Me_3SbS	$Me_2InX.L$	Cl	75
	$MeInX_2.L$	Cl	75
	$Et_2InX.L$	Cl,Br	75
2,2',2''-Terpyridine	$MeInX_2.L$	Cl	69

* From tensimetric studies.

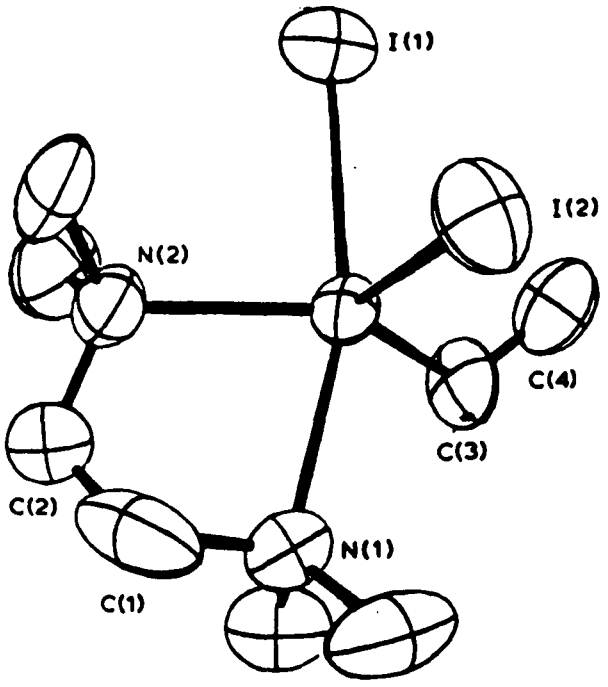


Diagram 7. Molecular structure of $EtInI_2(TMEDA)$.[71]

For the other known complexes very little information is available. The 1,2-diaminoethane and 2,2'-bipyridyl adducts with Me_2InX (X=Cl,I) have been shown by molecular weight determinations to be monomeric in nitromethane solutions.[69]

One of the complexes is particularly unusual and deserves mentioning. The triphenylphosphine adduct $(Me_2InCl)_2PPh_3$ has been prepared but very little is known of its properties. It has been proposed, on the basis of very little evidence, that it has an ionic structure of formulation $[Me_2In.PPh_3][Me_2InCl_2]$.[59]

Organoindium Compounds.

The co-ordination chemistry of the organoindium compounds has previously been comprehensively reviewed [3] and so the following is

only a summary of the general situation for these co-ordination compounds.

As is common for most group 13 element compounds trialkylindium compounds will readily form complexes with electron donors. These are almost always 1:1 complexes, with the exception of the compound $In(C_6F_5)_3$ which can accommodate two ligands.[76] Some *X*-ray crystallographic studies have been carried out on these complexes and have shown that they generally have an approximately tetrahedral geometry around the indium. A typical example is the complex formed between trimethylindium and 2,2,6,6-tetramethylpiperidine whose structure has been determined and is shown in Diagram 8.[77]

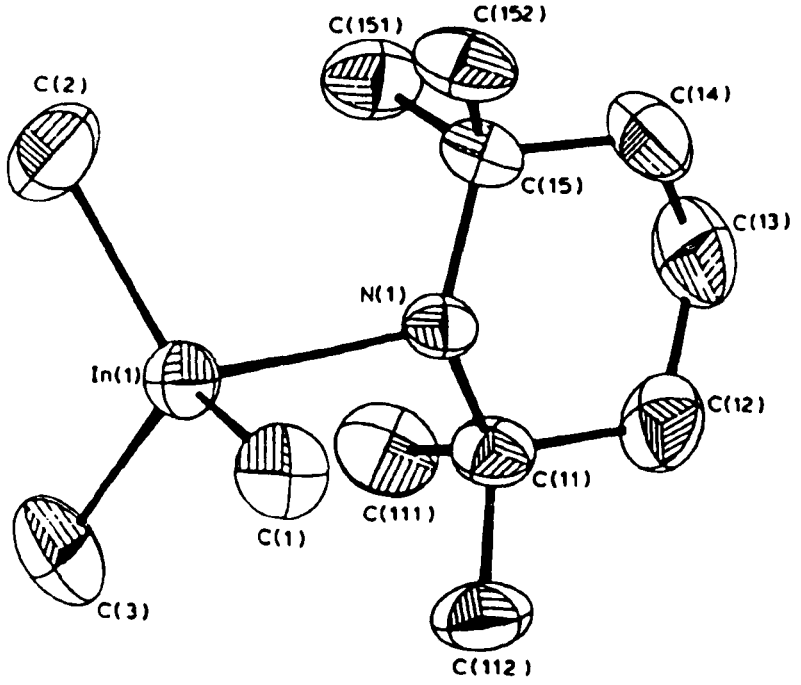


Diagram 8. Molecular structure of the 2,2,6,6,-tetramethylpiperidine complex with trimethylindium.[77]

Organoindium compounds have been shown to be very reactive towards a range of compounds containing different functional groups, including compounds containing protonic hydrogen atoms and those

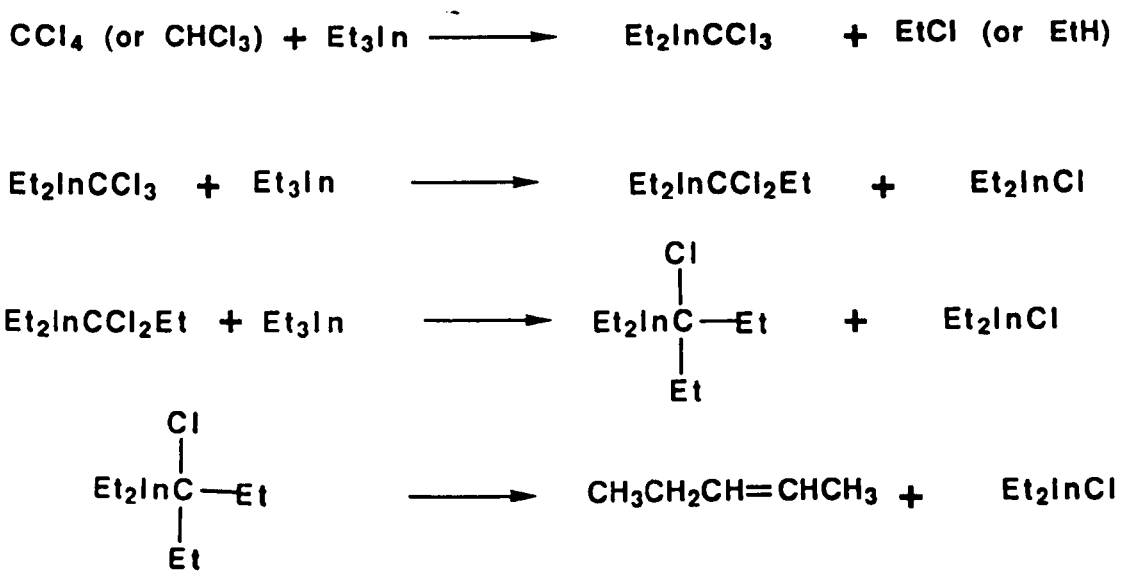
containing heteronuclear double bonds. These are discussed in more detail below.

Reactions of Organoindium Compounds Involving Cleavage of Indium-Carbon Bonds.

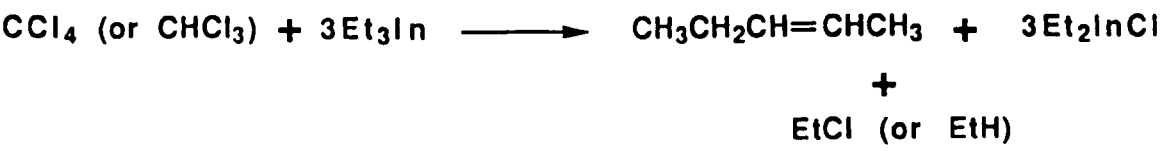
Triethylindium has been shown to react readily with a range of halogenated compounds to give the corresponding diethylindium halide. These reactions are high yielding (>70%) and occur slowly at room temperature but more quickly on warming in hexane solution.[7 8]

$$Et_3In \xrightarrow[\left(\begin{array}{c} or\ CHCl_3 \\ CH_2X_2 \\ (X=Br,I) \end{array}\right)]{CCl_4} Et_2InX$$

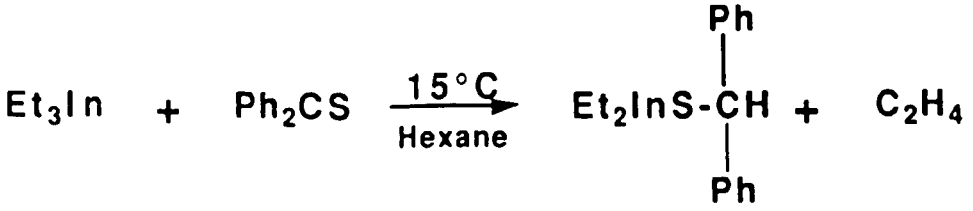
The pathway of these reactions is unclear, but it is believed (in the case of chloroform and carbon tetrachloride) to involve successive reactions with the formation of one equivalent of Et_2InCl at each step. The overall reaction and the pathway involved are believed to be represented by the following equations.



Overall Equation:-

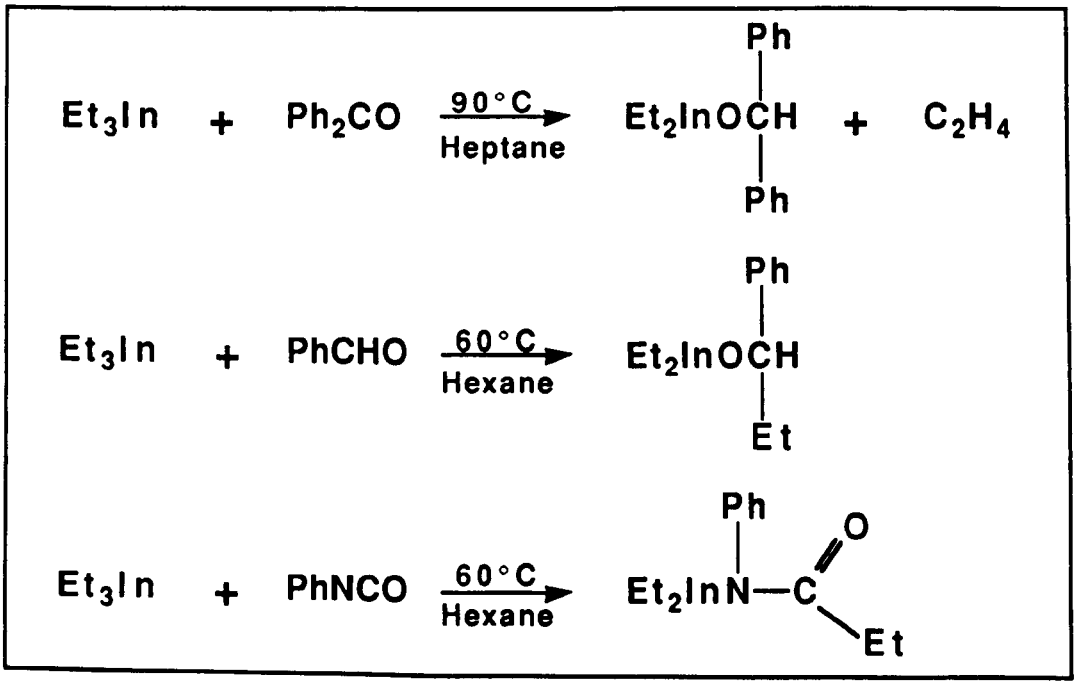


An interesting reaction was found to occur between triethylindium and thiobenzophenone. This produced ethene and a compound containing an indium-sulphur bond in 78% yield.[79]

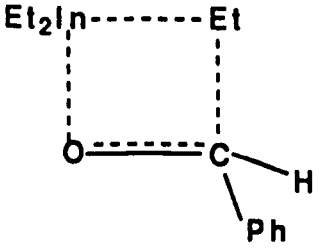


Subsequently, triethylindium was found to react with three other species containing heteronuclear double bonds, benzophenone, phenylisocyanate and benzaldehyde.[80] The reaction with benzophenone proceeded in the same manner as that for thiobenzophenone with elimination of ethene. However, the reactions with benzaldehyde and phenylisocyanate gave rise to products resulting

from what appeared to be an alkyl migration reaction, although nothing was reported to suggest a mechanism. Interestingly no reaction was observed to occur with benzonitrile (except for the formation of a complex). These reactions are represented by the following equations:-

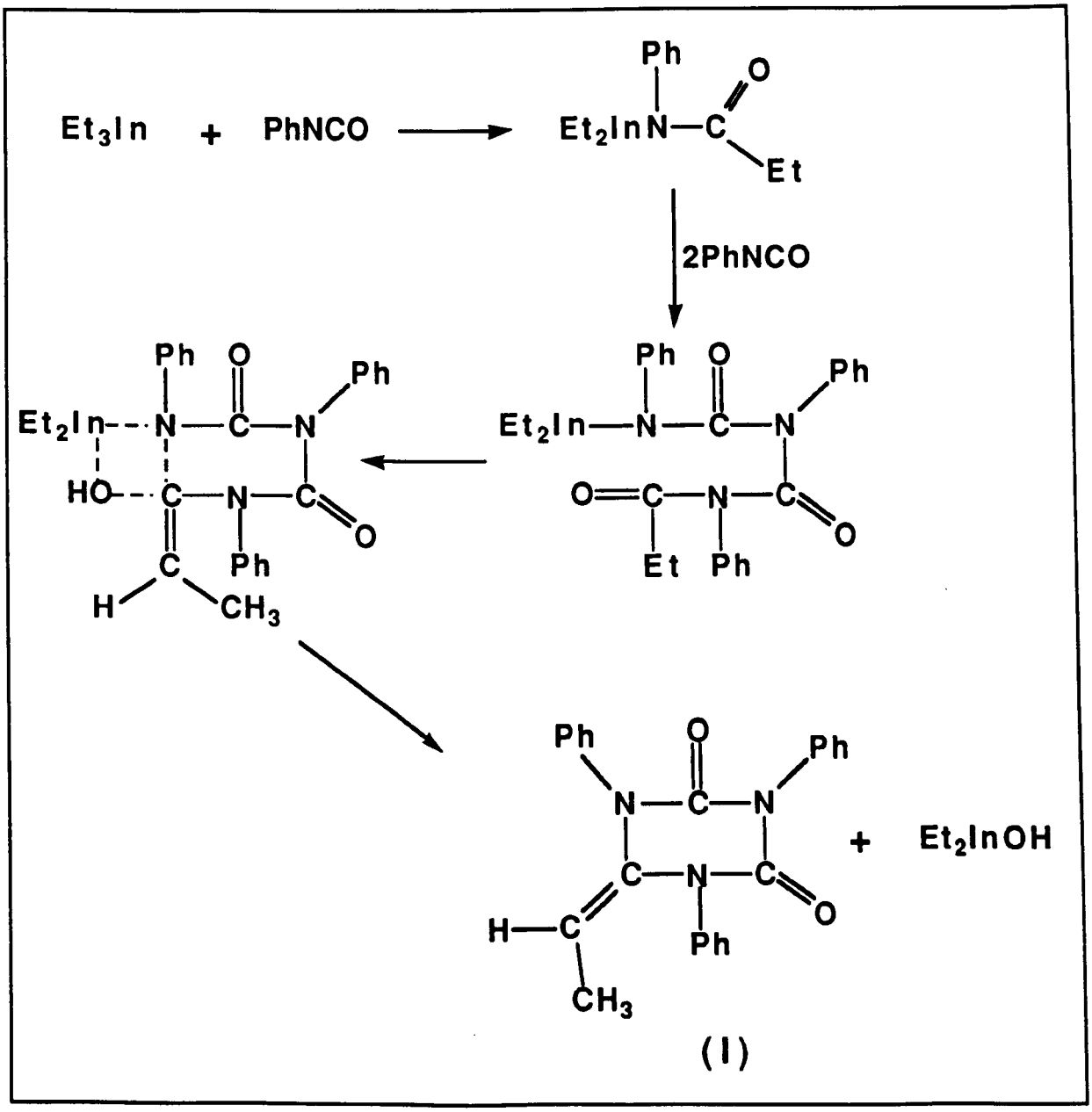


Although no mechanisms were proposed for these reactions it is conceivable that, in the case of the reaction with benzaldehyde that the reaction proceeds via a transient intermediate of the following type:-



The reaction with phenylisocyanate was studied in more detail and the product was found to undergo further complex reactions in the presence of excess phenylisocyanate. These were found to yield a cyclic

triazine (I). The reaction scheme for the formation of this compound that was proposed (without any real evidence) is shown below.[81]



Indium-carbon bonds have also been shown to be susceptible to insertion reactions. Thus, trimethylindium will react with liquid sulphur dioxide at -45 °C to give $(MeSO_2)_3In$ in high yield.[82]

$$Me_3In + 3SO_2 \xrightarrow{-45°C} (MeSO_2)_3In$$

Reactions of Organoindium Compounds with Compounds Containing Protonic Hydrogen Atoms.

Trialkylindium compounds react very readily with compounds containing protonic hydrogen atoms with the elimination of alkane and the formation of an indium derivative. This reaction is usually clean and almost quantitative. As such it represents an ideal method of preparing novel organometallic derivatives of indium.

Such reactions have been shown to occur for a wide range of substrates including alcohols, carboxylic acids, alkynes, phosphines amines and thiols. The compounds that have been prepared by this method are shown in Table 8. It is clear from this data that the vast majority of these compounds are the result of the elimination of only one equivalent of alkane, that is they have the general formula R_2InL. As a general rule it has been found that for the majority, the reaction will go no further than this stage and that the addition of excess reagent in an attempt to cause the elimination of more than one equivalent of alkane has (with a few exceptions) no effect. This observation is matched by the surprising stability of the $[R_2In]^+$ cations, which are stable even in aqueous solution. The compound $(Me_2In)_2SO_4$ (produced from the reaction of anhydrous H_2SO_4 with two equivalents of trimethylindium)[123] can be dissolved in water without hydrolysis of the indium-carbon bonds to give a solution containing $[Me_2In]^+$ cations.[123] The stability of these cations can also be seen in the mass spectra of organoindium compounds. In the mass spectrum of

Table 8. Reactions of Organoindium Compounds with Protonic Species.

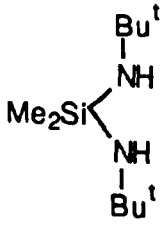
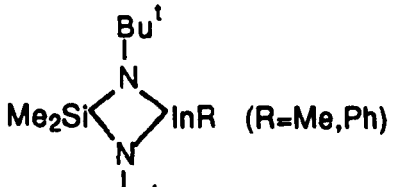
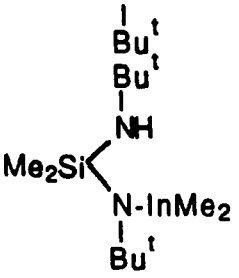
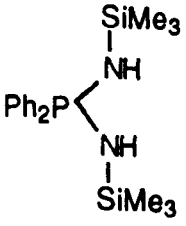
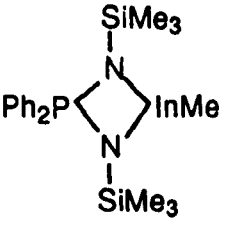
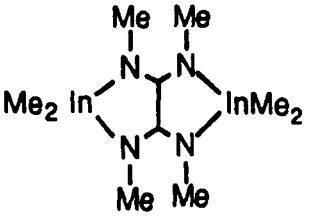
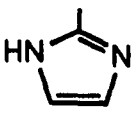
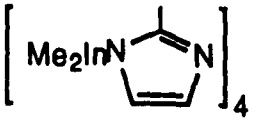
Reagent	Product	Ref.
R_2NH	$(Me_2InNMe_2)_2$	83
	$(Me_2InNR_2)_2$ (R=Et,Pr^i,Me_3Si)	84
	$(Me_2InNPhMe)_2$	85
R_2PH	$(Me_2InPR_2)_3$ (R=Me,Et)	86
	$(Et_2InPEt_2)_3$	87
	$(Me_2InPR_2)_2$ (R=Ph,Bu^t)	84
Me_2AsH	$(Me_2InAsMe_2)_3$	86
$PhPH_2$	"MeInPPh"?	86
$PhAsH_2$	"MeInAsPh"?	86
$MeAsH_2$	"MeInAsMe"?	86
NH_3	$(Me_2InNH_2)_n$	83
PH_3	InP	88,89
	$(MeInPH)_n$	90
		91
		92
		93
N,N'-Dimethyloxamidine		127
		94

Table 8. (Cont'd).

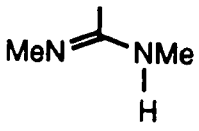
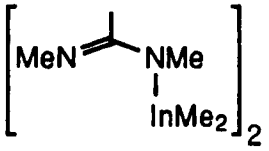
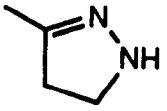
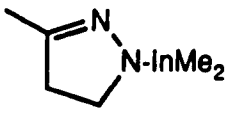
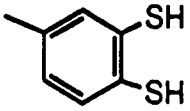
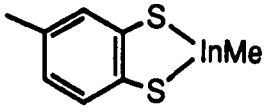
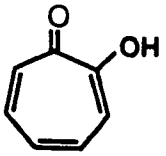
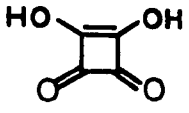
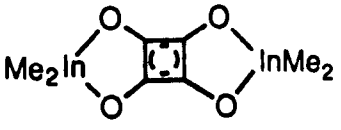
Reagent	Product	Ref.
		95
		96
ROH	Bu^n_2InOR (R=Bu^t,Ph)	97
	Me_2InOMe	83
	$(Me_2InOBu^t)_2$	92
R_3SiOH	$(R_3SiOInMe_2)_2$ (R=Me,Ph)	92
MeSH	$(Me_2InSMe)_2$	83
		98
RSH	$In(SR)_3$ (R=Et,Pr^n,CH_2Ph)	99
	Ph_2InSR (R=Et,Pr^n,Bu^t,CH_2Ph)	99
RCO_2H	Bu_2InO_2CR (R=Et,Ph)	97
	$In(O_2CR)_3$ (R=Et,Pr^i,Bu^t)	100
	Me_2InO_2CR (R=CF_3,Me)	69,101
	Et_2InO_2CR (R=Me,Et)	102
	Ph_2InO_2CMe	103
	Ph_2InO_2CMe	103
2-Ethylhexanoic Acid (HL)	Bu_2InL	97
 (HL)	Me_2InL	104
		105
HO_2PX_2 (X=F,Cl,H)	$(Me_2InO_2PX_2)_2$	106
HO_2EMe_2 (E=P,As)	$(Me_2InO_2EMe_2)_2$	107
HS_2PMe_2	$(Me_2InS_2PMe_2)_2$	108
MeC(O)SH	$Et_2InS(O)CMe$	109

Table 8. (Cont'd).

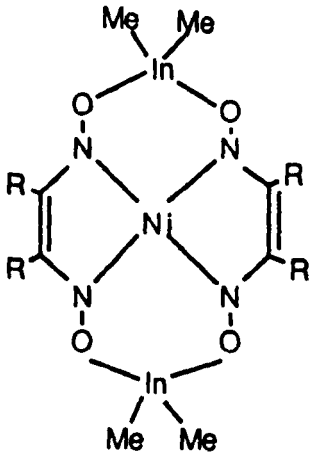
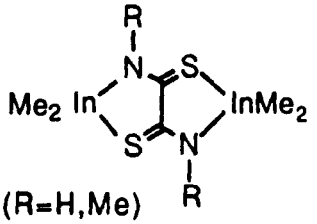
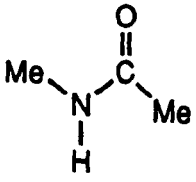
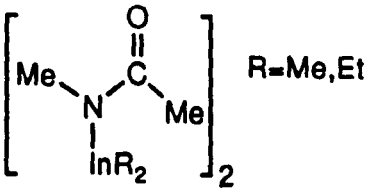
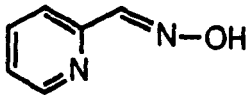
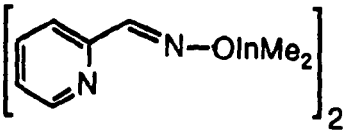
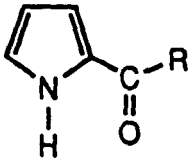
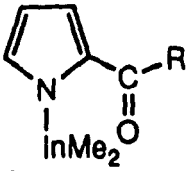
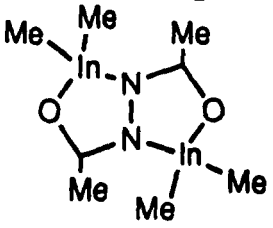
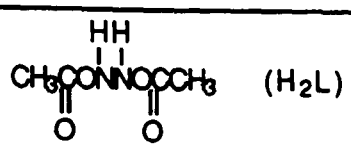
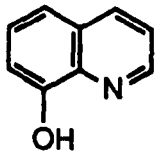
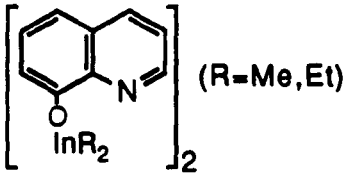
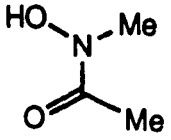
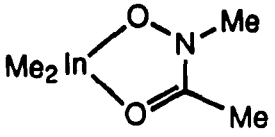
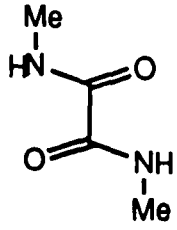
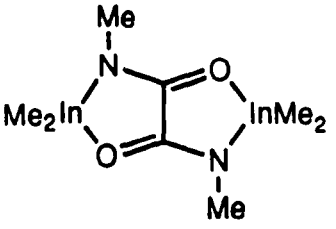
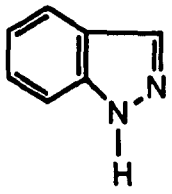
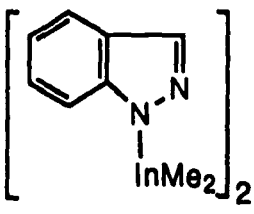
Reagent	Product	Ref.
$[R_2C_2N_2(O)OH]_2Ni$ R=H,Me		110
Dithiooxamide *N,N'*-Dimethyldithiooxamide	 (R=H,Me)	111
	 R=Me,Et	80
$Me_2C{=}NOH$	$[Me_2C{=}NOInMe_2]_2$	112
		113
 (R=H,Me)		114
1,2-Diacetylhydrazine		115
$Me_2NCH_2CH_2OH$	$Me_2NCH_2CH_2OInR_2$ (R=Me,Et)	116

Table 8. (Cont'd).

Reagent	Product	Ref.
 (H_2L)	$(Me_2In)_2L$	3
	 (R=Me,Et)	116
		117
		118
C_5H_6 (CpH)	Me_2InCp	119
CH_3NO_2	$R_2InCH_2NO_2$ (R=Me,Et)	120
$HC(Me_2)NO_2$	$Et_2InC(Me_2)NO_2$	120
PhC≡CH	PhC≡CInMe$_2$	121
Acetylacetone (acacH)	$Bu_2In(acac)$	97
$B_{10}H_{14}$	$[Me_2In][B_{10}H_{12}InMe_2]$	122
HCl(g)	$MeInCl_2$	69
H_2SO_4 (anhyd)	$(Me_2In)_2SO_4$	123
H_2O	"$MeIn(OH)_2$"	124
		96

trimethylindium, the main ion occurs at m/z=145 which corresponds to the $[Me_2In]^+$ cation.[125] However, it is worth noting that several reactions do go further than the elimination of one equivalent of alkane (some of these are discussed in the following sections). In general terms, however, the overall picture is confused, and generalisations concerning the extent of the reaction that would occur for a particular reagent cannot easily be made.

The product of the reaction between trimethylindium and water has not been properly identified. It has, however, been shown that water causes two equivalents of methane to be eliminated at room temperature.[124] It has also been reported that the product of this reaction is $MeIn(OH)_2$, but no evidence for this was published.[126] This observation appears to contradict the reported stability of the $[Me_2In]^+$ cation in aqueous media discussed above and so this reaction with water would therefore appear to merit further study.

Amines, Phosphines and Arsines.

All of the reactions that have been reported to occur between the indium trialkyls and compounds of the type R_2EH (E=N,P,As) have resulted in the elimination of only one equivalent of alkane even in the presence of excess R_2EH. For the amines (R_2NH) all of the known products are dimeric. This has been shown by *X*-ray crystallographic studies on a series of such compounds which were all found to contain an In_2N_2 ring with two dialkylamido groups bridging between two indium atoms, $[(Me_2InNR_2)_2$; R=Me,Et,Pr^i,$Me_3Si]$.[84] Similar dimeric products have been found for the reactions between trimethylindium and Ph_2PH or $Bu^t{}_2PH$.[84] However, the products with less sterically

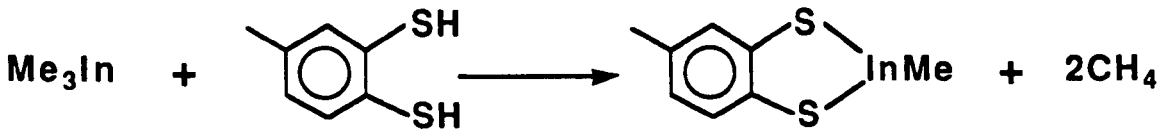
congested phosphines such as Et_2PH and Me_2PH are believed to be polymeric in the solid state and trimeric in solution.[86,87] Similarly the product of the reaction with Me_2AsH has also been shown to be trimeric in solution, $[(Me_2InAsMe_2)_3]$.[86]

The reactions between trimethylindium and compounds containing more than one active hydrogen atom (REH_2 and EH_3) have been shown on heating to proceed as far as the complete elimination of two or three equivalents of alkane depending upon the reagent. Thus, $PhPH_2$, $PhAsH_2$ and $MeAsH_2$ react with trimethylindium to produce two equivalents of methane and polymeric products that could not be properly characterised.[86] Trimethylindium will react slowly with ammonia at room temperature but more rapidly on heating to 70 °C to form the polymeric compound $(Me_2InNH_2)_n$ which decomposes further on heating.[83] Phosphine (PH_3) will also react with trimethylindium at room temperature to give $(MeInPH)_n$ which decomposes (sometimes explosively) on heating to temperatures above 250 °C to give indium phosphide (InP).[90] The reaction between these two reagents at 700 °C is used to prepare semi-conducting indium phosphide .[88,89]

Alcohols and Thiols.

Trialkylindium compounds will react readily with alcohols to give the corresponding dialkylindium alkoxide and one equivalent of alkane. Thus, trimethylindium reacts with methanol to give Me_2InOMe and one equivalent of methane even at temperatures just above the melting point of methanol(-98 °C).[83] It is noteworthy that this compound was found to be trimeric in benzene solution. Similarly tri-*n*-butylindium has been shown to react with alcohols to produce analogous compounds

of the type Bu_2InOR (R=Ph,Bu^t).[97] Trimethylindium will also react with MeSH to give a product that is, in contrast to the product with methanol, dimeric in benzene solution, $[(Me_2InSMe)_2]$.[83] Toluene-3,4-dithiol will react with trimethylindium at room temperature to eliminate two moles of methane and to yield the corresponding dithiolate[98]:-

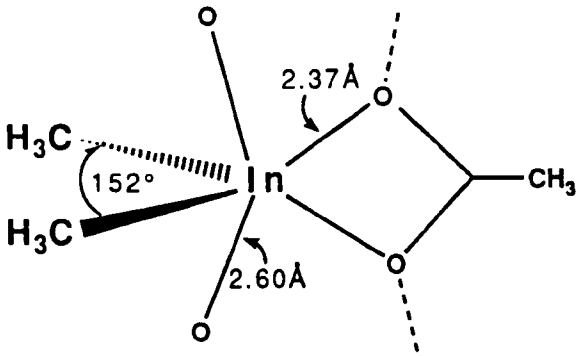


Carboxylic and Thiocarboxylic Acids.

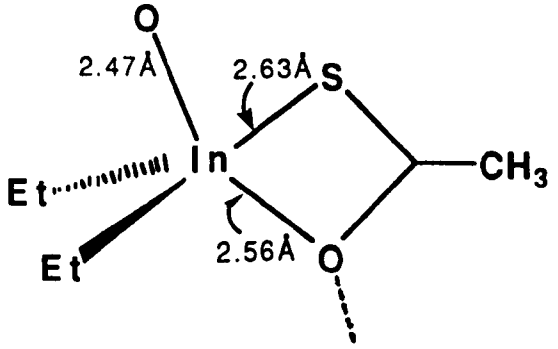
Trimethylindium has been shown to react readily with a range of carboxylic acids with elimination of methane to form polymeric materials. With one equivalent of acid these reactions proceed to the dimethylindium derivative, however, with excess acid the reaction proceeds with evolution of three equivalents of methane to form products of general formulation $In(O_2CR)_3$ (from HO_2CR; R=Et,Pr^i,Bu^t). Little is known about these compounds other than that their low solubilities indicate a polymeric structure.[100]

An *X*-ray crystallographic study of the product of the reaction between trimethylindium and acetic acid, Me_2InCO_2Me, has shown that the structure consists of a bidentate acetate group with both oxygen atoms bonded to the same indium atom. The molecules are linked together in chains in such a manner that the indium atoms attain six co-ordination. The indium atoms not only have two carbon atoms and two

oxygen atoms bonded directly to them but also have two longer range interactions with two oxygen atoms of neighbouring molecules[101]:-



Triethylindium has been shown to react with thioacetic acid to produce the compound $Et_2InOSCCH_3$. The *X*-ray crystal structure of this compound showed that the compound is polymeric, as is the case for dimethylindium acetate described above. However, for thioacetic acid the indium atoms are only five co-ordinate. They are bonded directly to two ethyl groups and both the oxygen and the sulphur atoms of a bidentate thioacetate group. In addition to these the indiums are bonded only to one oxygen atom of a neighbouring molecule to produce chains. No secondary bonding occurs through the sulphur atoms[109]:-



Derivatives Containing Both Nitrogen and Oxygen Atoms.

Several of the reactions summarised in Table 7 are with protonic species containing both oxygen and nitrogen atoms. It has generally been found that the products of these reactions have indium with a co-ordination number of four, five or six depending upon the nature of the product. This can be achieved by either inter- or intra-molecular association (or a mixture of both). This behaviour is exemplified by the two products of these reactions that have had their structures determined by *X*-ray cystallographic methods. These are discussed in more detail here. The references for the other reactions of this type are given in Table 7.

Trimethylindium will react with pyridine-2-carbaldehyde oxime in a 1:1 ratio at room temperature to produce a dimeric product. One equivalent of methane is eliminated in the reaction, the proton coming from the -OH group of the reactant. The structure of this compound has been determined by an *X*-ray crystallographic study. The indium atoms in this compound were found to be five co-ordinate in a distorted trigonal bipyramidal environment consisting of two carbon atoms, two nitrogen atoms and one oxygen atom. The structure consists of five fused rings, and the whole molecule is folded along its middle so that the two halves are at an angle of 55° to each other.[113] This can be seen more clearly in Diagram 9.

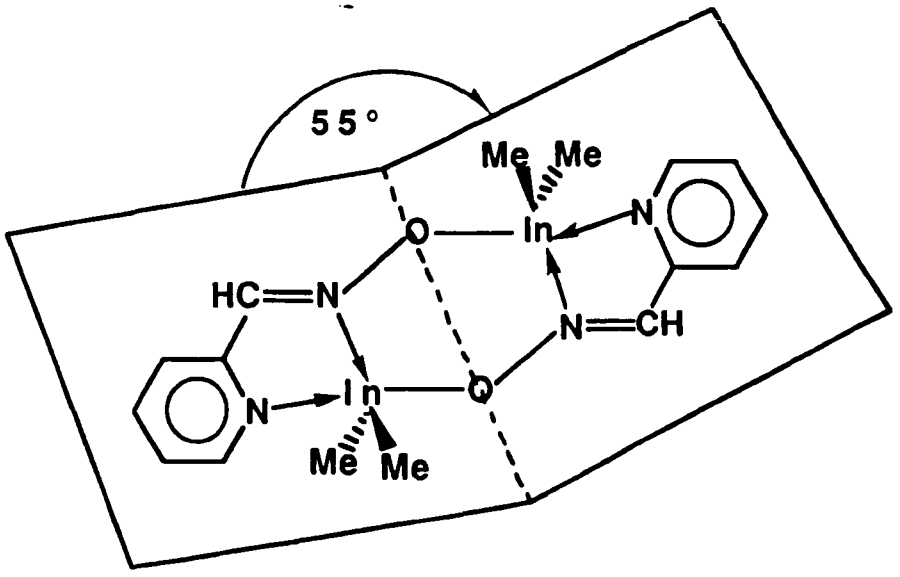


Diagram 9. Structure of the pyridine-2-carbaldehyde oxime derivative of trimethylindium.

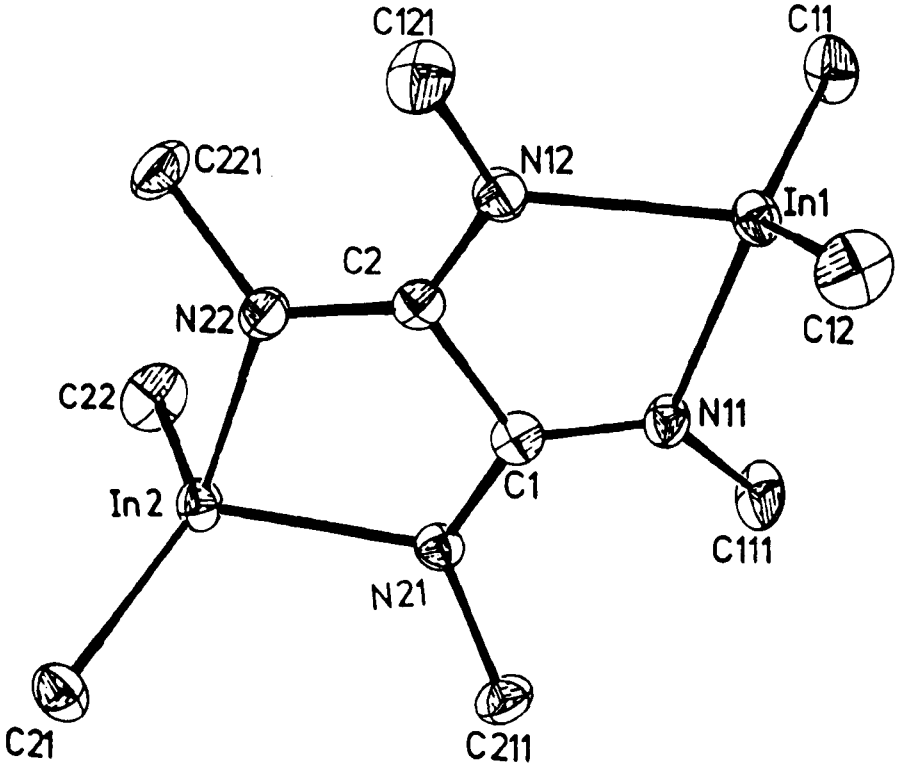


Diagram 10. Molecular structure of the tetramethyloxamidine derivative of trimethylindium.[127]

Two equivalents of trimethylindium have been shown to react with one equivalent of tetramethyloxamidine (H_2L) to produce a compound containing two dimethylindium units, $(Me_2In)_2L$. The *X*-ray crystal structure of this compound showed that the indium atoms are in an approximate tetrahedral environment with two nitrogen and two carbon atoms bonded to each.[127] This structure is shown in Diagram 10.

Reactions with other Protonic Species.

Trimethylindium will also react with species which have a protonic hydrogen bonded to a carbon atom. Thus, nitromethane reacts with trimethylindium at room temperature to produce methane and the compound $Me_2InCH_2NO_2$.[120] Similarly, acetylacetone readily looses its acidic hydrogen atom to react with trimethylindium to form $Me_2In(acac)$ and methane.[83]

An interesting reaction occurs between trimethylindium and decaborane(14). In this reaction two equivalents of trimethylindium react with one equivalent of decaborane(14) at room temperature to produce two equivalents of methane and an indium-borane derivative in 96% yield. The structure of the product has not been determined by *X*-ray diffraction techniques, however, the ^{1}H-n.m.r. and ^{11}B-n.m.r. spectra and the conductivity in solution were all consistent with an ionic product of formulation $[Me_2In][B_{10}H_{12}InMe_2]$. It is believed that the anion in this compound is a dodecahydro-*nido*-decaborate(2-) anion acting as a four electron ligand to a $[Me_2In]^+$ cation.[122]

Volatility is an important property for precursors for the preparation of indium phosphide. The compounds need to be volatilised

prior to their use in the MOVPE process and so any novel precursor must not be involatile. This presents particular problems for the preparation of precursors containing both an indium and a phosphorus atom. Such compounds contain both acceptor (indium) and donor (phosphorus) atoms, and so readily form oligomers or polymers via In-P-In linkages. This in turn leads to a reduction in volatility. Some work has shown that the use of sterically congested constituents in these compounds can limit this tendency towards oligomerisation. This topic is discussed further below.

Control of Oligomerisation Using Sterically Hindered Substituents.

Compounds of gallium or indium containing phosphido or arsenido groups are usually associated or polymeric. For example, $(Me_2GaPMe_2)_n$ and $(Me_2InPMe_2)_n$ have been shown to be polymeric glasses.[86] Similarly, attempts at preparing compounds containing three phosphido groups such as $In(PPh_2)_3$ have resulted in the formation of intractable polymeric materials.[128] It has , however, been shown that the use of very sterically hindered substituents around the metal and/or phosphorus atoms limits the ability of the compound to form M-P-M linkages and so limits the degree of oligomerisation that occurs. The reaction between $(Me_3SiCH_2)_3In$ and diphenylphosphine has been shown to proceed with elimination of one equivalent of tetramethylsilane and the formation of the corresponding diphenylphosphido indium compound, $(Me_3SiCH_2)_2InPPh_2$.[55] Unlike similar compounds with less bulky substituents this was shown to be

dimeric, with bridging phosphido groups, the structure of which is shown in Diagram 11.

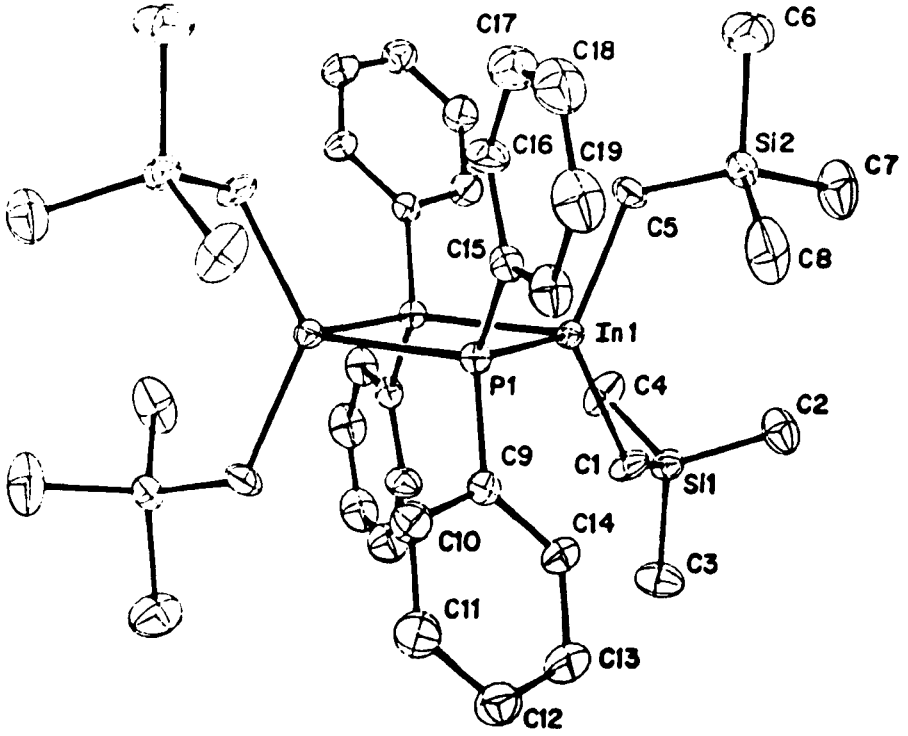
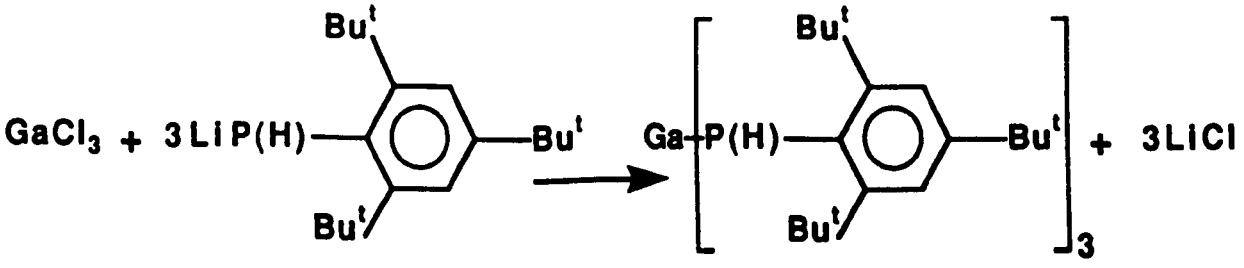


Diagram 11. View of the molecular structure of $[(Me_3SiCH_2)_2InPPh_2]_2$. The thermal ellipsoids are drawn at 30% probability level.[55]

It has also been possible to synthesise a monomeric gallium species by the use of bulky phosphido groups,[129] according to the following equation:-

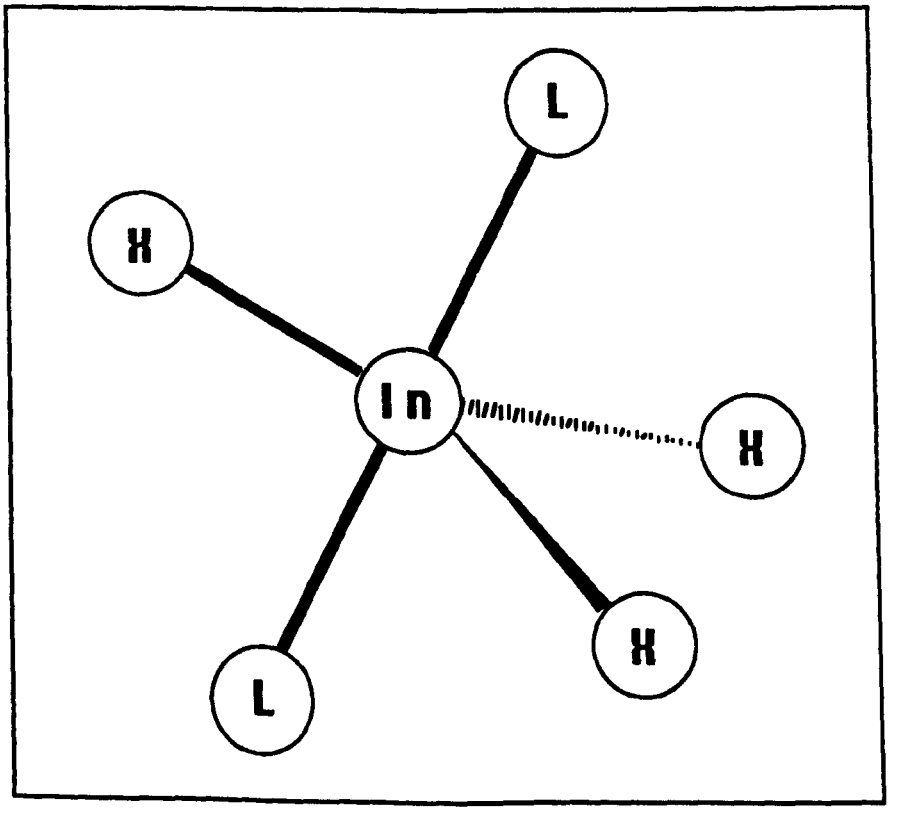


A crystallographic study of this compound was attempted but a complete solution was not obtained. It was, however, reported that the monomeric nature of the compound could be discerned. Similarly the use of $LiPBu^t_2$ produced the analogous gallium compound, $Ga(PBu^t_2)_3$ although in this case no structural evidence was reported.[129]

Clearly, a detailed study of some co-ordination compounds of the indium trihalides with particular emphasis on furthering our knowledge of the solid state structures and solution behaviour of such compounds would be extremely useful. In addition our knowledge concerning the reactions of the indium trialkyls and the properties of organoindium compounds containing phosphorus is by no means comprehensive and merits further investigation. It would also be of interest to examine the possibility of whether monomeric phosphido-indium derivatives can be prepared in the manner that has already been discussed (above) for gallium, in view of the greater size of indium atoms (*ca.* 0.18 Å larger ionic radius for indium than gallium).

CHAPTER 2

CO-ORDINATION CHEMISTRY OF THE INDIUM TRIHALIDES



Introduction.

The work on co-ordination chemistry that is discussed in this chapter is concentrated on phosphine complexes for reasons already stated. Specifically, however, the work has been concentrated on the phosphine complexes of indium triiodide. The main reason for this is that so little is known about these complexes in comparison to the complexes of the trichloride and the tribromide. This is evident not only from the lack of *X*-ray crystallographic studies but also from interpretational difficulties encountered in studies of the vibrational spectra of these complexes. This is best demonstrated by some examples. The vibrational spectra of the 1:2 complexes formed between the indium trihalides and trimethyl- and triethyl-phosphine have been reported. For the trichloride and tribromide complexes the Raman spectra are relatively simple in the range for the In-X stretching modes and consequently it was concluded with a reasonable degree of certainty that these complexes have a *trans*-trigonal bipyramidal environment around the indium atoms. However, in the case of the complexes formed between these phosphines and indium triiodide the Raman spectra in the expected range for the In-I modes (100-200cm^{-1}) were much more complicated and it was concluded that an assignment of their structure on the basis of these spectra was impossible.[19] A similar situation was found for the 1:1 complexes formed with tricyclohexylphosphine (which has already been discussed in Chapter 1, page 27).[19]

It was also pointed out in the Chapter 1 that only one phosphine complex with an indium trihalide has had its structure determined by a single-crystal *X*-ray diffraction study. The triphenylphosphine complex, $InCl_3.(PPh_3)_2$, was shown to have a trigonal-bipyramidal

structure.[38] None of the 1:2 complexes formed between indium triiodide and phosphine ligands have yet been shown to have a trigonal bipyramidal arrangement of the ligands around the indium.

Some 1:1 phosphine complexes with indium triiodide have been reported. As has already been mentioned (Chapter 1, page 27) the indium triiodide complex formed with tricyclohexylphosphine is believed to be ionic on the basis of interpretations of its Raman spectrum.[19] Similarly the complexes formed between tri-*p*-tolyl-phosphine or tri-*p*-methoxyphenyl-phosphine and indium triiodide have been shown to be ionic in solution and are believed to have the formulation $[I_2In(PR_3)_2][InI_4]$.[24]

Mono-Phosphine Complexes of Indium Triiodide.

During the course of this work it was found that the addition of a single equivalent of a phosphine ligand ($HPBu^t_2$, $HPCy_2$, $HPPh_2$, PBu^i_3) to a diethylether solution of one equivalent of indium triiodide caused a series of 1:1 complexes to precipitate. While this may not appear to be at all unexpected, it is not always the case that a complex with the stoichiometry expected from the mole ratio of reactants used is obtained, as other studies reported below will demonstrate. Thus the addition of two equivalents of each of the phosphine ligands to a diethylether solution of indium triiodide also produced the same 1:1 complexes. No evidence was found for the formation of 1:2 complexes with any of these phosphines. These complexes were highly crystalline and colourless and could be further purified by recrystallisation from hexane or toluene. They were all slightly sensitive to moisture, decomposing over a period of several hours when exposed to air. Their

^{1}H-n.m.r. spectra confirmed the presence of the phosphine ligand and their identity as 1:1 complexes was confirmed by microanalyses (C,H,I).

An *X*-ray crystallographic study of the di-*t*-butylphosphine complex was carried out. This showed that this complex has a monomeric structure based upon a tetrahedral arrangement of the ligands. The molecular structure that was determined is shown in Diagram 1. It can be seen that the complex has a staggered ethane type conformation and that both the indium and the phosphorus atoms have approximate tetrahedral environments, as is discussed below in more detail. The hydrogen atoms were not located in this study. The hydrogen atom attached to the phosphorus atom was inserted with an approximate P-H bond length of 1.4 Å for diagrammatic purposes. The complete list of bond lengths and angles for this compound is given in Appendix B (page 189). The In-P bond length of 2.586(6) Å falls within the range of known In-P bond lengths and is discussed in relation to these and the other values found later in this work in Appendix A (page 170). The P-C bond lengths have a mean value of 1.87 Å, which can be compared to those in the similar compound $GaCl_3.PMe_3$ which have a mean value of 1.79 Å.[130] The slightly longer P-C bond length found for the $Bu^t_2P H$ complex is consistent with the increased steric congestion around the phosphorus atom in this structure. The In-I bonds in this compound have a mean length of 2.67 Å which compares well with the length of the terminal In-I bonds in the In_2I_6 dimer which have a mean value of 2.64 Å.[5]

Of particular interest in this structure is the way in which the molecules pack together. The packing of the molecules in the unit cell is shown in Diagram 2. There are two types of intermolecular interactions in this structure. There is a long range In-I interaction and a weak hydrogen bond between an iodide and the P-H group (located when this

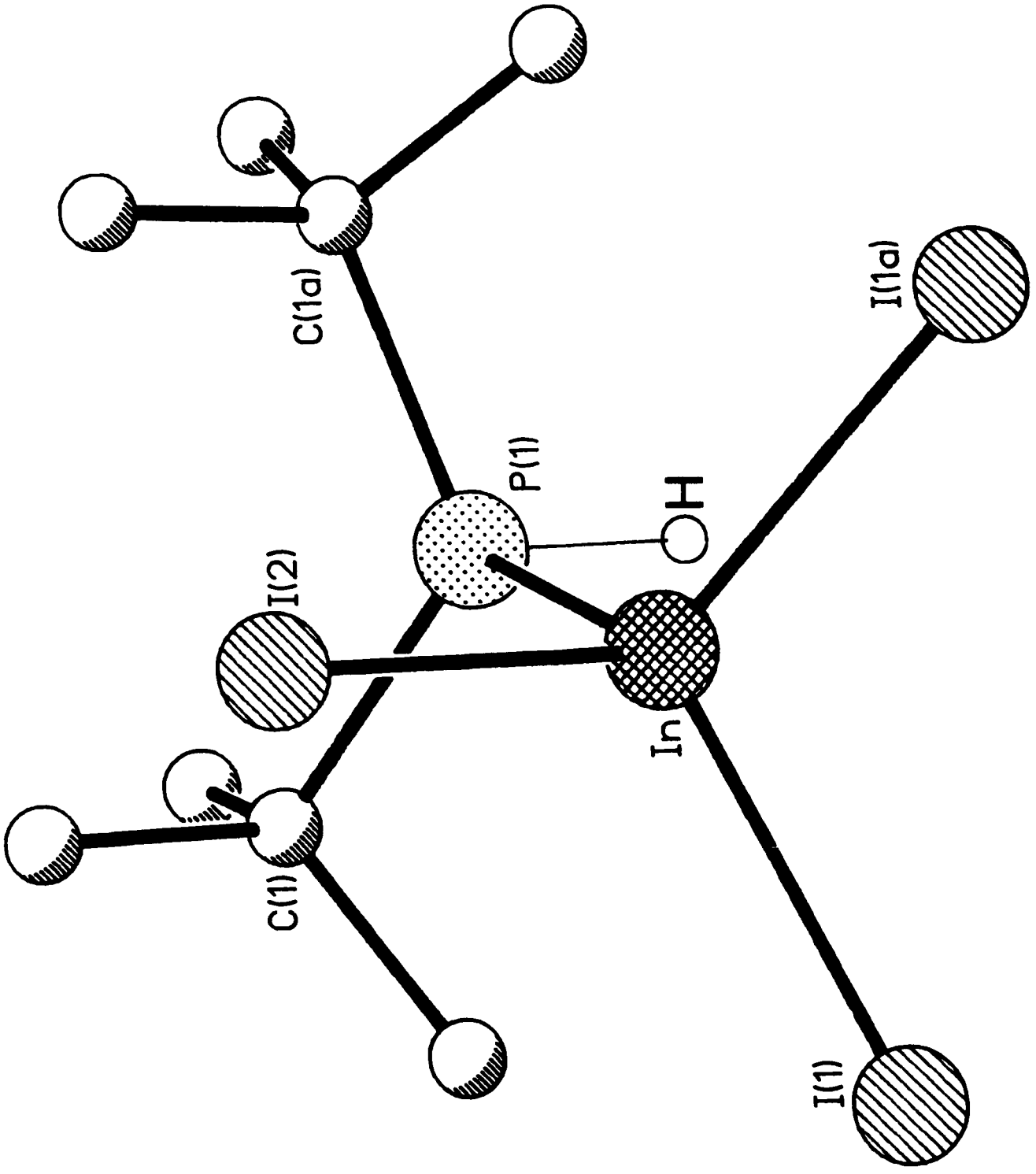


Diagram 1. View of the molecular structure of $I_3In.HPBu^t_2$ as determined by a single-crystal *X*-ray diffraction study. [Selected bond lengths (Å);In-I(1), 2.668(2), In-I(2), 2.679(2), In-P(1), 2.586(6), P(1)-C(1), 1.870(25). Selected bond angles (°); I(1)-In-I(2), 107.7(1), I(1)-In-P(1), 113.7(1), I(2)-In-P(1), 106.7(1), I(1)-In-I(1a), 107.0(1)]

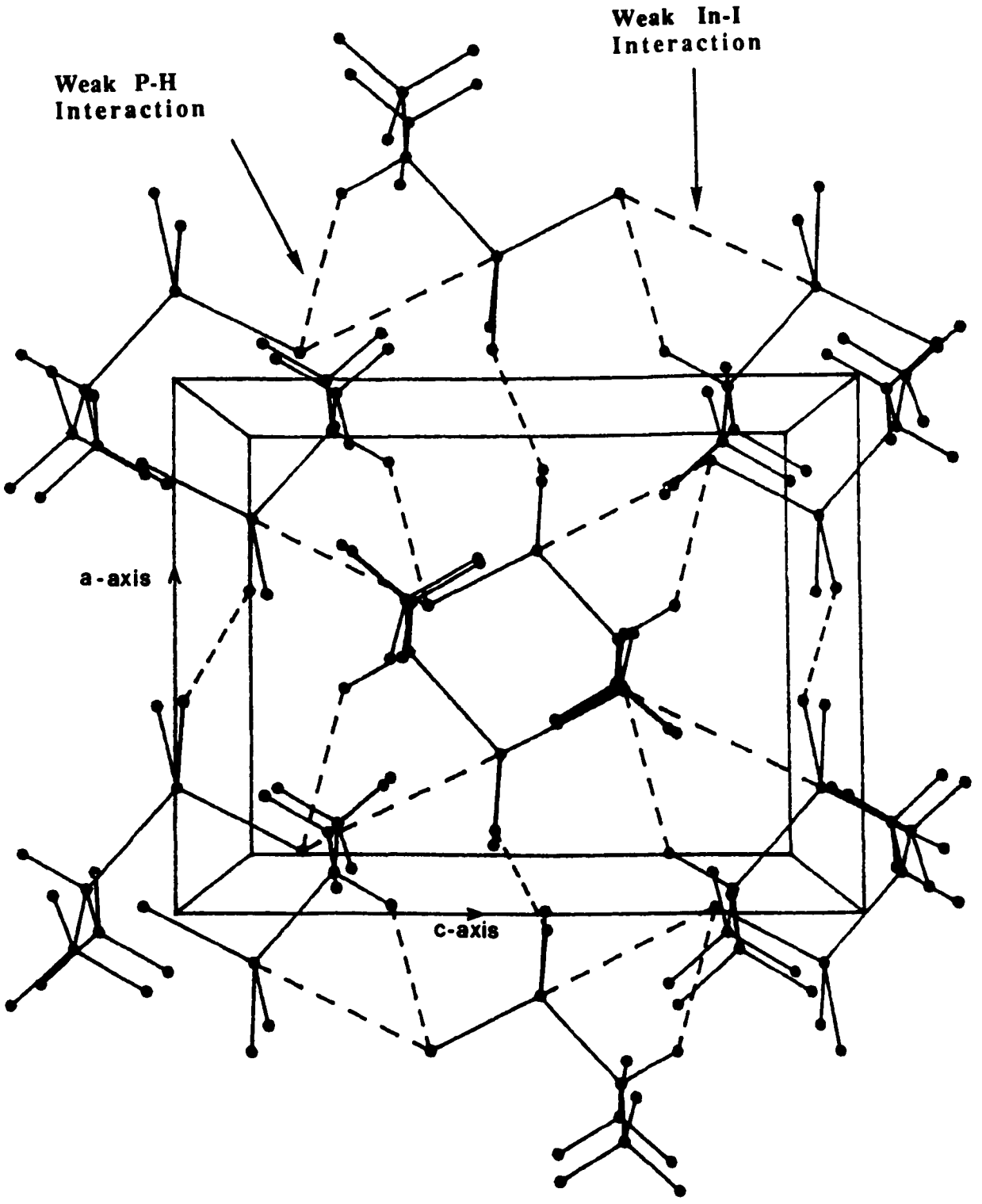


Diagram 2. Packing diagram for the structure of $I_3In.HPBu^t_2$. The view shown is along the *b*-axis of the unit cell.

hydrogen atom is inserted in the fourth tetrahedral site of the phosphorus atom). A close-up view of the way in which two of these molecules interact with each other is shown in Diagram 3. Each indium atom has a long range interaction with an iodide of a neighbouring molecule making the metal pseudo five co-ordinate. This indium-iodine interaction has a length of 4.25 Å [In(a)-I(2b)] compared with the sum of the van der Waal's radii of an indium and iodine atom which is 4.43 Å.[131] This indium-iodine interaction is, therefore, approximately 0.18 Å less than a van der Waal's interaction. It is, however, only just strong enough to distort the tetrahedral arrangement around the indium atom. The three iodides bonded directly to the indium atom are compressed together by this interaction and have bond angles between them (I-In-I) of on average 2° less than the ideal tetrahedral angle of 109.5°. There is also a small increase in In-I bond length for the iodide that is involved in this interaction. This has a length of 2.679(3) Å as opposed to the shorter length of 2.668(3) Å found for the other In-I bonds. This is consistent with a slight reduction in electron density around the iodine atom (through the secondary interaction) giving rise to a weakened In-I bond.

There also appears to be a weak form of hydrogen bonding present in the structure. This occurs between the hydrogen atom attached to the phosphorus atom and one of the iodides of a neighbouring molecule. The estimated position of this hydrogen atom leads to a value of approximately 3.1 Å for the iodine-hydrogen separation. The sum of the van der Waal's radii for a hydrogen and iodine atom is also approximately 3.1 Å.[131] There is also no indication that there is such an interaction from the infra-red spectrum which shows a band that can be assigned as a P-H stretch at 2364 cm^{-1}. Although this is somewhat shifted from the expected position for this

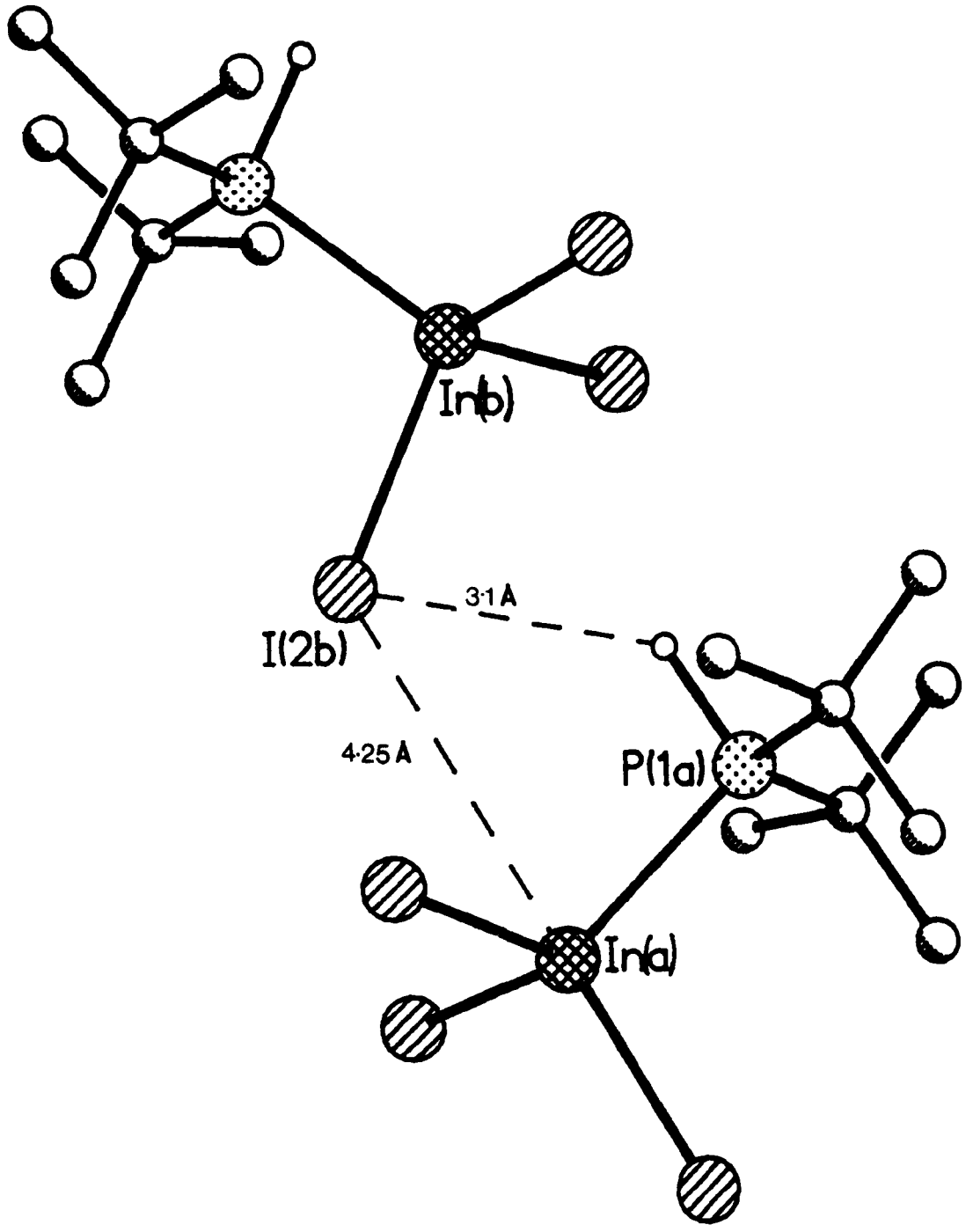


Diagram 3. View of the way in which two molecules of $I_3In.HPBu^t_2$ interact in the crystal. The long range In-I and H-I interactions can be seen.

band (2270-84 cm^{-1})[4] this may simply be a result of the co-ordination to the indium. Clearly, this hydrogen bond is extremely weak and in view of the uncertainty of the position of the hydrogen atom it is questionable whether it constitutes a genuine interaction or not.

As has already been mentioned, a study of a similar complex between indium triiodide and tricyclohexylphosphine has previously been reported. The complexity of the Raman spectrum of this complex made structural conclusions difficult, but it was proposed that it has an ionic structure, $[I_2In(PCy_3)_2][InI_4]$.[19]

For the purposes of comparison the Raman spectrum of the But_2PH complex prepared in this work was obtained from a powder sample. This spectrum also showed a complex series of bands in the expected range for In-I and In-P stretches (100-200 cm^{-1}). The complexity of this spectrum makes it impossible to assign any bands to particular In-I or In-P modes. The spectrum, in this region, is summarised in Table 1. Also given for comparison are the bands in the Raman spectrum of $I_3In.PCy_3$ which has previously been published.[19]

There are several similarities between the Raman spectrum of $I_3In.HPBut_2$ and $I_3In.PCy_3$, including the band at *ca.* 184 cm^{-1}. For $I_3In.PCy_3$ this band was assigned previously as the ν_3 stretching mode of the $[InI_4]^-$ anion. However, a major difference between the two spectra is the absence of the strong band at *ca.* 140 cm^{-1} in the spectrum of $I_3In.HPBut_2$. This band was assigned as the ν_1 stretching mode of the $[InI_4]^-$ anion. The absence of this band from the spectrum of this complex is in agreement with the non-ionic structure that was found by *X*-ray crystallography.

Table 1. Comparison of the bands (cm^{-1}) observed in the Raman spectrum of $I_3In.HPBu^t_2$ in the region expected for In-I and In-P stretching modes with those previously reported for $I_3In.PCy_3$.[19]

$I_3In.HPBu^t_2$	$I_3In.PCy_3$
117(w)	138(s)
151(w)	
162(w)	162(w)
184(w)	185(m)
195(w)	191(w)
	198(w)
	220(w)
	320(w)

The Raman spectra of the other three complexes prepared in this work (Cy_2PH, Ph_2PH and PBu^i_3) were also obtained from powder samples. These are shown in Diagram 4. These three spectra are all very similar to each other and show clear differences from the spectrum of the di-*t*-butyl phosphine complex. The most outstanding difference is that each of these spectra exhibits a strong band in the range 135-145 cm^{-1}. As was mentioned above this band was taken as evidence of the presence of the $[InI_4]^-$ anion in the case of the tricyclohexyl phosphine complex. However, none of these spectra exhibits the weak accompanying band at *ca.* 185 cm^{-1}.

The conclusion to be drawn from these Raman spectra is that these latter three complexes all have the same structure and that that structure is different to that found for the di-*t*-butyl phosphine

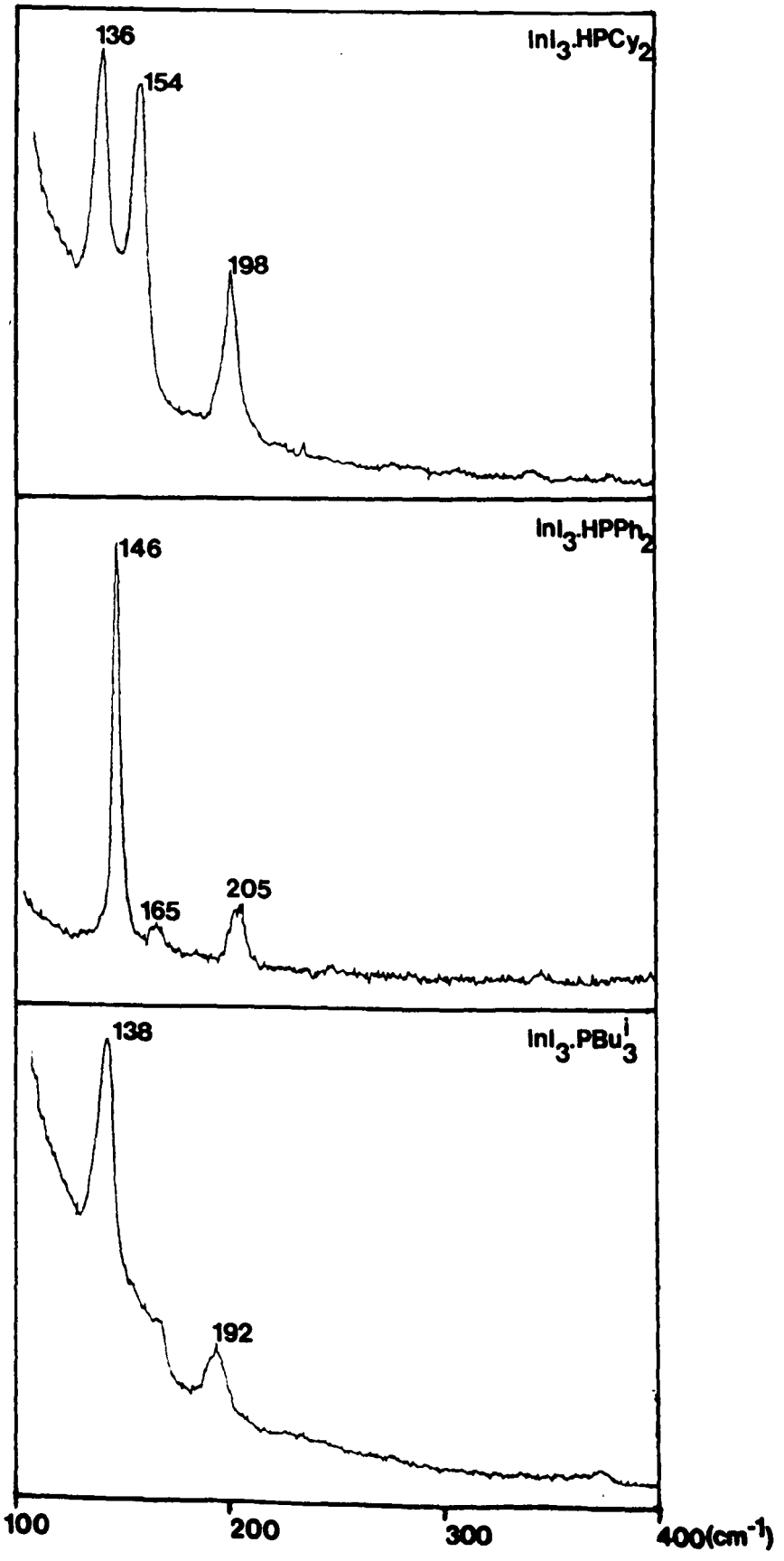


Diagram 4. Raman spectra (100-400 cm^{-1}) of the indium triiodide-phosphine adducts.

complex. The band in the range 135-145 cm^{-1} may be indicative of an ionic structure for these complexes.

To test the validity of these conclusions based upon the Raman spectra, the molecular structure of the diphenylphosphine complex was determined by a single-crystal *X*-ray diffraction study. The structure that was determined is shown in Diagram 5. The bond lengths and angles for this complex are given in Appendix B (page 199). **The structure is remarkably similar to that of the di-*t*-butyl phosphine complex.** This complex is also a covalent monomer with an approximate tetrahedral environment around the indium and phosphorus atoms. The mean In-I bond length is 2.67 Å which is identical to the value found for $I_3In.HPBu^t_2$. Both of these values compare well with the mean length of 2.64 Å found for the terminal In-I bonds in the In_2I_6 dimer.[5] The P-C bonds in this complex have a mean length of 1.80 Å which is close to the value of 1.87 Å already found for $InI_3.Bu^t_2PH$. The In-P bonds have a mean length of 2.60 Å which again is in the expected range and is discussed in more detail in Appendix A (page 170).

At first sight, then, this structure appears to contradict the evidence obtained by Raman spectroscopy, which predicted different structures for these complexes. However, on closer examination of the structure of $I_3In.HPPh_2$ some significant differences can be found to the structure of $I_3In.HPBu^t_2$. The secondary interactions between molecules in the two structures are quite different. $I_3In.HPPh_2$ does not have in the solid state the long range indium-iodine interactions or the very weak hydrogen bonding that were found in the structure of $I_3In.HPBu^t_2$. Instead, there are some long range iodine-iodine interactions. The way in which these molecules pack together in the unit cell is shown in Diagram 6. A close up view of the interactions between three of these molecules is shown in Diagram 7. The two I-I

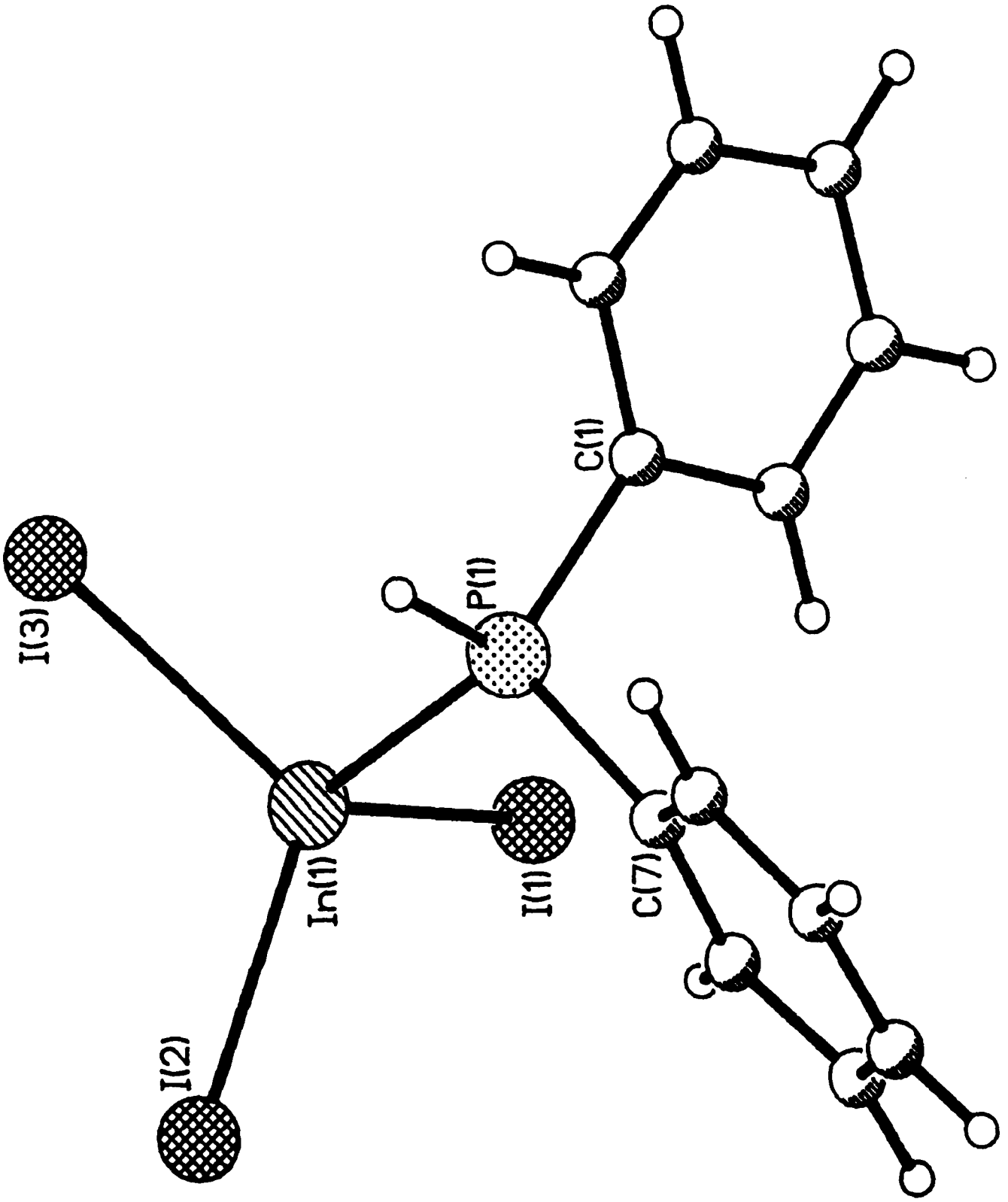


Diagram 5. View of the molecular structure of $I_3In.HPPh_2$ as determined by a single-crystal *X*-ray diffraction study. [Selected bond lengths (Å); In(1)-I(1), 2.674(5), In(1)-I(2), 2.676(5), In(1)-I(3), 2.672(5), In(1)-P(1), 2.605(9). Selected bond angles (°); I(1)-In(1)-I(2), 114.3(1), I(1)-In(1)-I(3), 114.3(1), I(2)-In(1)-I(3), 113.1(1), I(1)-In(1)-P(1), 102.8(2).]

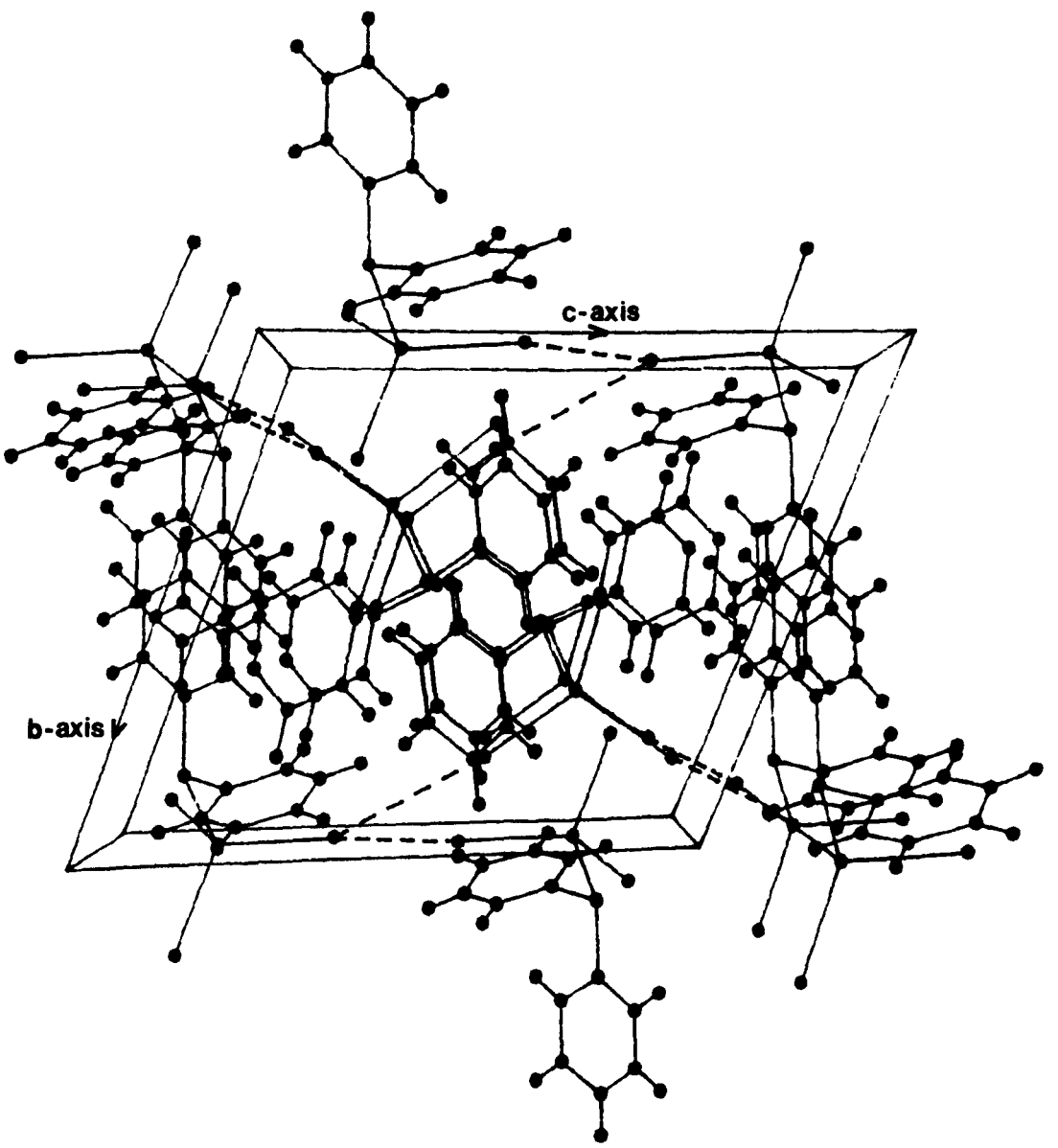


Diagram 6. Packing diagram for the crystal structure of $I_3In.HPPh_2$. The view shown is along the *a*-axis.

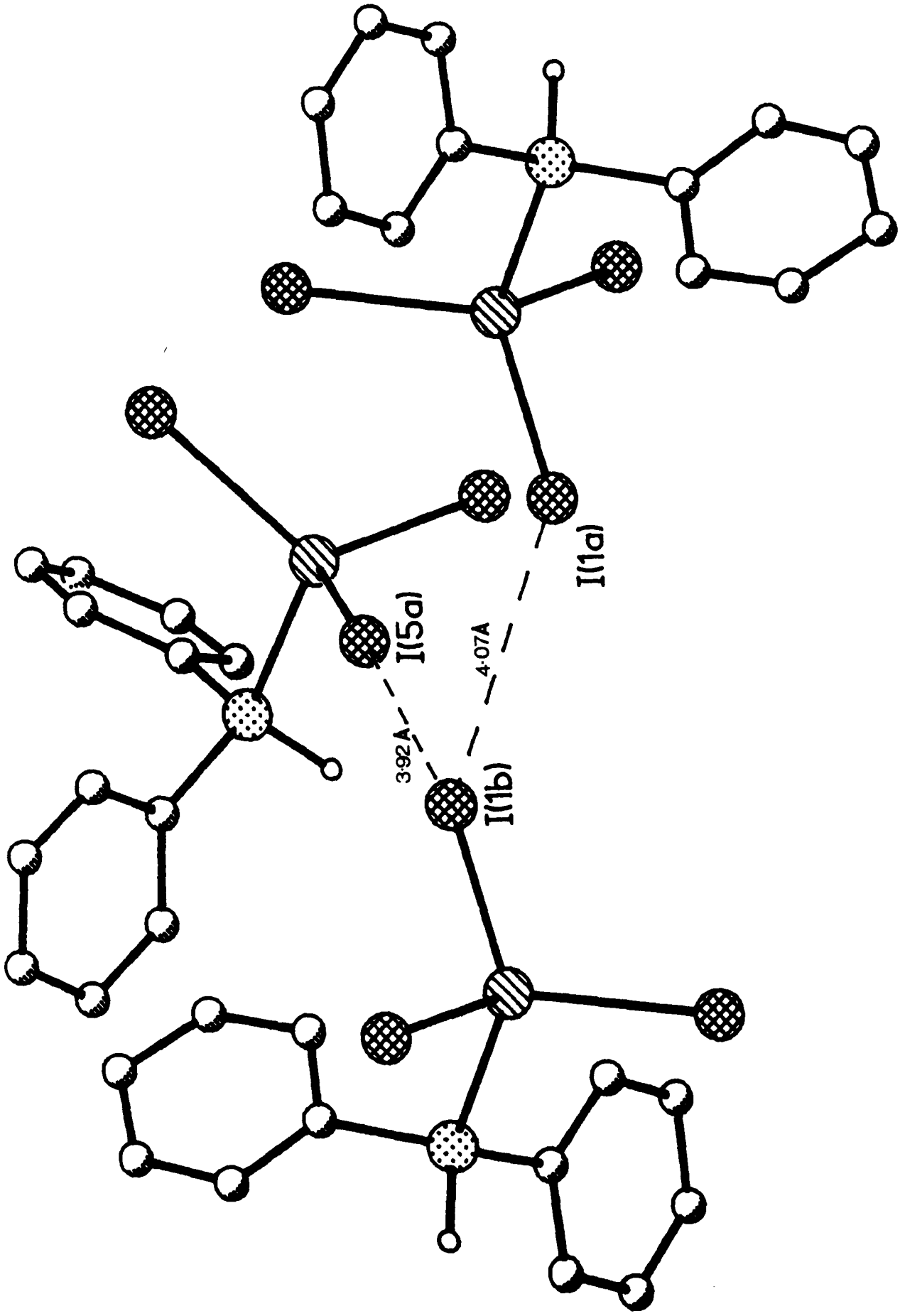


Diagram 7. View of the way in which three molecules of $I_3In.HPPh_2$ interact in the crystal. The long range I-I interactions can be seen.

interactions that were found have distances of 4.07 and 3.92 Å. These are approximately equal to the sum of the van der Waal's radii for two iodine atoms which is 3.96 Å.[131] This shows that, although there is an interaction between these iodine atoms it is very weak. These interactions can be compared to those in the structure of the In_2I_6 dimer. In this compound the mean distance separating iodine atoms in different molecules is 4.35 Å and the shortest such distance is 4.11 Å.[5] Thus, the shortest such distance in the structure of $InI_3.HPPh_2$ is almost 0.2 Å shorter than the shortest such distance in the In_2I_6 dimer. Iodine-iodine interactions have been shown to occur between molecules of solid iodine (I_2) in which there are weak intermolecular I-I bonds with mean lengths of 3.50 Å.[132] So in comparison to these, the interactions in $I_3In.HPPh_2$ are very weak. They are also weaker than the In-I interactions in the structure of $I_3In.HPBu^t_2$ in which the interactions were strong enough to give rise to a change in In-I bond length. In the structure of $I_3In.HPPh_2$ the I-I interactions are not strong enough to give rise to a similar change in In-I bond length.

The different types of secondary interactions that are found in the two structures can be used to account for the very different Raman spectra of the two complexes. The frequency of a vibrational mode involving the iodide ligands would be strongly affected if those iodides are involved in secondary bonding with neighbouring molecules. These would give rise to a change in In-I bond strength but of equal importance a lowering of the symmetry of the molecule. Hence, the differing interactions in $I_3In.HPPh_2$ and $I_3In.HPBu^t_2$ give rise to different Raman spectra.

The reasons for these different long range interactions are unclear. There is no obvious correlation between the donor strength of the phosphine and the structure of the complex. Although the pK_a

values for these ligands are specifically concerned with the co-ordination of a proton, these values can be used as a rough guide in comparing ligand strengths. The pK_a values for the four phosphine ligands studied in this work are shown in Table 2.[133] The phosphine that gives the complex with the different structure ($HPBu^t_2$) has an intermediate pK_a value.

Table 2. Values for the pK_a's of the phosphine ligands used to prepare InI_3 complexes.[133]

Phosphine	pK_a
PBu^i_3	7.97
$HPBu^t_2$	*
$HPCy_2$	4.55
$HPPh_2$	0.03

* the value for $HPBu^t_2$ is unknown, however, the similar phosphine $HPBu^i_2$ has a pK_a of 4.11.

Alternatively the steric bulk of the phosphines involved may govern the way in which the complexes can pack together and so affect the intermolecular interactions that are possible. The steric demands of these ligands can be quantified in terms of the "cone angle" approach of Tolman.[134] In this approach the "cone angle" of a ligand is the angle of a cylindrical cone that would just enclose the phosphine ligand. For the phosphine ligands used in this work, this approach gives values for the "cone angles" of 128° (Ph_2PH), 142° (Cy_2PH), 143° (PBu^i_3) and 150° (Bu^t_2PH). This shows that of the phosphines used, the bulkiest is $HPBu^t_2$.

This is consistent with the fact that the complex of this phosphine is the "odd one out" in terms of crystal structure.

Surprisingly, no $^{31}P\{^{1}H\}$-n.m.r. spectra for any indium trihalide-phosphine complexes have been previously reported. In an effort to investigate the potential of this technique the $^{31}P\{^{1}H\}$-n.m.r. spectra of the phosphine complexes prepared in this work and of the previously prepared triphenylphosphine complex ($I_3In.PPh_3$)[20] were obtained.

With the exception of the diphenylphosphine complex, these spectra were all unusual in that the observed signals all had very large line widths. The half height line widths and chemical shifts of these signals are summarised in Table 3.

Table 3. $^{31}P\{^{1}H\}$-n.m.r. **Data** of the $I_3In.PR_3$ complexes showing the chemical shifts and the half-height line widths ($\Delta\nu_{1/2}$).

Complex	δ (ppm)[a]	$\Delta\nu_{1/2}$ (Hz)
$I_3In.PBu^{i}_3$	-34	2200
$I_3In.HPBu^{t}_2$	3	1300
$I_3In.HPCy_2$	-33	800
$I_3In.PPh_3$	-22	800
$I_3In.HPPh_2$	-48	50

[a]Relative to H_3PO_4 (external). Spectra run as $CDCl_3$ solutions.

The large values found for these line widths is unusual in that other phosphine complexes such as $MeInI_2.PR_3$ and $Me_2InI.PR_3$

(discussed in Chapter 3) give lines with half-height line widths of 50 Hz or less. There are two possible explanations for these broad signals. Either they are the result of an exchange process in solution or they are due to quadrupolar coupling to the indium.

In an attempt to identify the cause, the variation of the spectrum with temperature was studied. For the complexes with $HPBu^{t}_{2}$ and PBu^{i}_{3} the width of the signals was found to remain almost unchanged on heating up to 80 °C. However, on cooling, the signals were found to sharpen. In the case of the PBu^{i}_{3} complex, the signal had a half-height line width of 350 Hz at 193 K. The spectra for this complex are shown in Diagram 8.

If the broad signals observed for these complexes were the result of an exchange process in solution then on cooling, the signal should have broadened and eventually as the process slowed, separated into signals corresponding to the different phosphorus containing species involved in the process (provided that the rate of exchange slows to less than the n.m.r. time scale). This does not appear to be the case. The alternative to this is coupling to the quadrupolar indium nucleus. The most abundant indium isotope is ^{115}In which has an abundance of 95% and a nuclear spin of 9/2. Coupling between this and the phosphorus in the complexes would give rise to a ten line multiplet. In practice, this would not be observed due to the very efficient relaxation caused by the quadrupole. The signals would each be broadened and if close enough to overlap would give rise to a single broad peak. On cooling, such a signal would be expected to sharpen. This is consistent with the observed spectra and so it can be concluded that the broad signals are the result of coupling to the indium. Although the diphenylphosphine complex, which gave a sharp signal, appears to be inconsistent with this

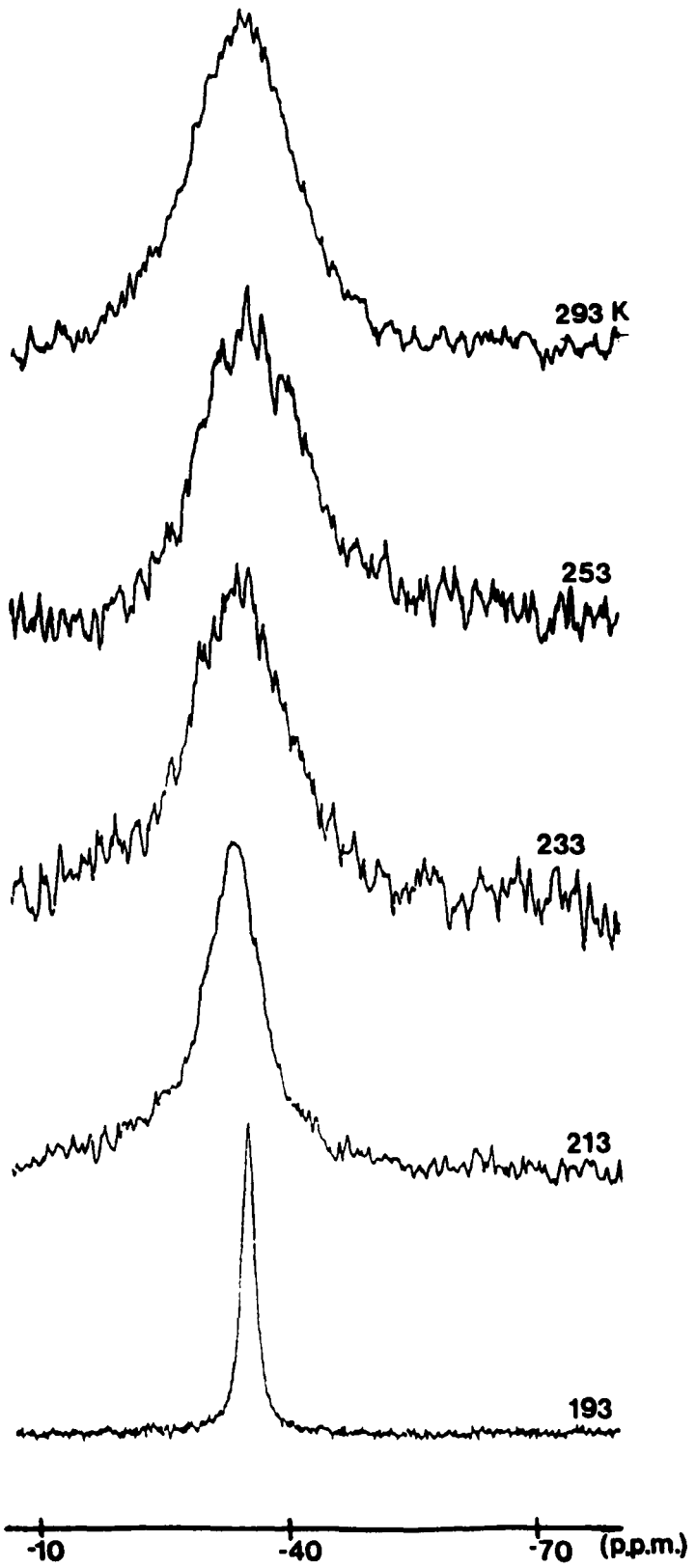


Diagram 8. Effect of cooling on the $^{31}P\{^{1}H\}$-nmr spectrum of $I_3In.PBu^i_3$. (d^8-toluene).

conclusion, this can be explained in terms of a different structure in solution for this complex and will be discussed later.

In order to obtain further information concerning the solution behaviour of these complexes, the effect of adding excess phosphine to a solution of a complex was studied using $^{31}P\{^{1}H\}$-n.m.r. spectroscopy. For a dichloromethane solution of $I_3In.HPBu^t_2$ and $HPBu^t_2$ in a 1:2 ratio only a single peak was observed at room temperature, showing that rapid exchange of bound and unbound phosphine occurs. The effect of cooling on this spectrum was studied. The resulting spectra are reproduced in Diagram 9. These show typical behaviour for two exchanging species in solution. On cooling the signal broadens and eventually below 190 K the signal separates into two. One of these signals corresponds to the free phosphine (+17 ppm) and the other corresponds to the complex (-1 ppm). These spectra also confirm that a 1:2 complex is not formed in solution. If such a complex was formed then on cooling, the signal corresponding to the complex would be shifted to a new position. The non-existence of such a complex is not too surprising in view of the steric bulk of the iodides and the phosphine.

These spectra give no information concerning the structure of the complex in solution. Previous work has shown that the 1:1 indium triiodide complexes of tri-*p*-tolylphosphine and tri-*p*-methoxyphenylphosphine as well as the analogous gallium complexes are ionic in polar solvents. They all have molar conductivity values of approximately half the value expected for a 1:1 electrolyte. However, if they are formulated as ionic dimers of the type $[I_2InL_2][InI_4]$, then the conductivity values are in the correct range for complete dissociation into a 1:1 electrolyte in solution.[24] Although it is not known how the degree of ionisation of these complexes varies with the nature of the solvent, it is likely that the complexes studied here using ^{31}P-n.m.r.

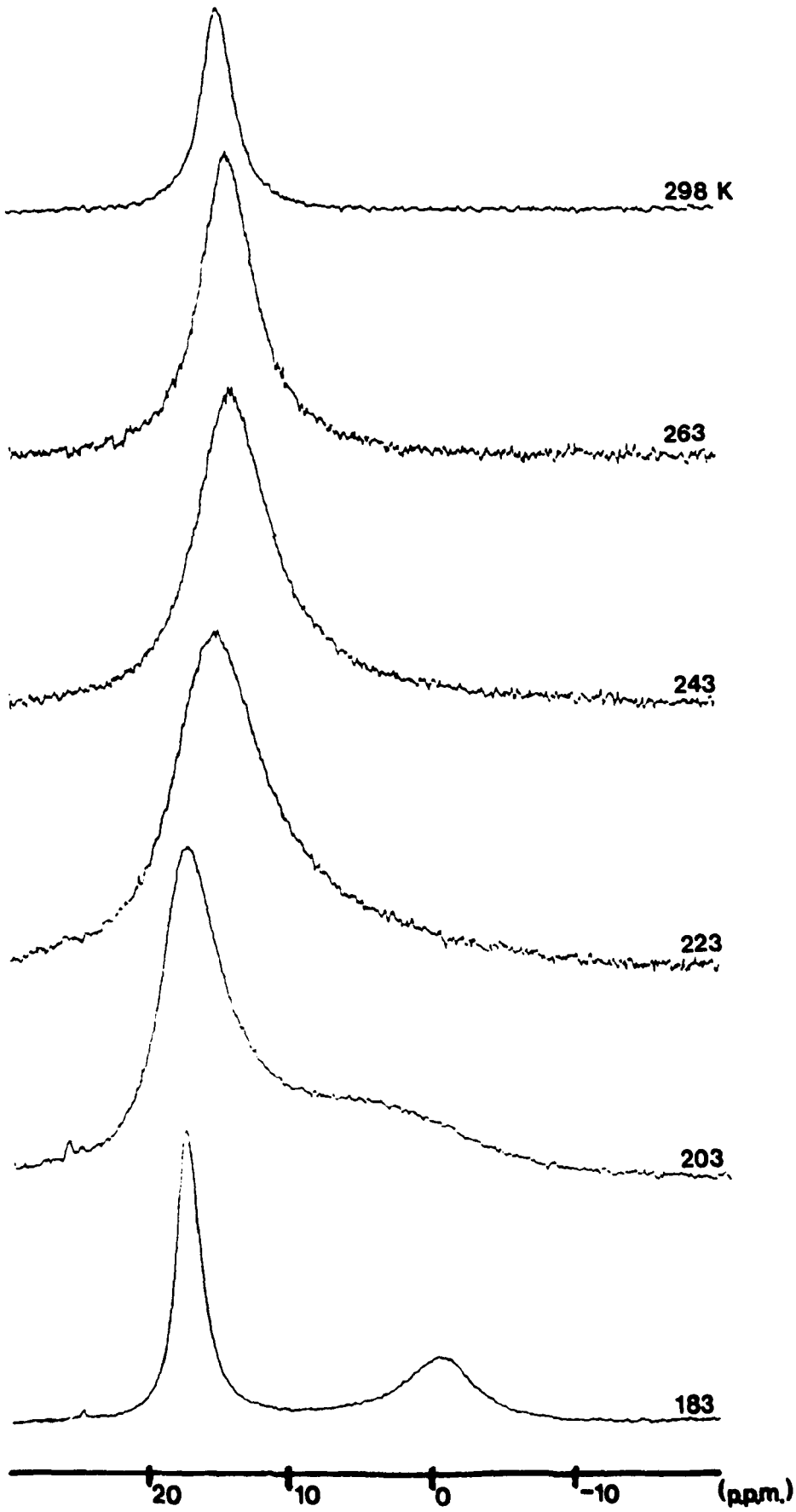


Diagram 9. Effect of cooling on the $^{31}P\{^{1}H\}$-nmr spectrum of a 2:1 mixture of $HPBu^{t}_{2}$ and $I_3In.HPBu^{t}_{2}.(CD_2Cl_2)$.

spectroscopy (in $CDCl_3$) are also ionic in solution. Some confirmation of this was obtained using ^{115}In-n.m.r. spectroscopy, the results of which are discussed later in this chapter. If these complexes are ionic dimers in solution, then the signals observed in the $^{31}P\{^{1}H\}$-n.m.r. spectra would correspond to the cation $[I_2In(PR_3)_2]^+$ and the exchange process observed would be the result of ligand exchange with this cation. For this process there are two possible mechanisms. An associative mechanism in which there is a five co-ordinate transition state or a dissociative mechanism in which there is a three co-ordinate transition state. These are represented by the following equilibria.

Associative:

$$[I_2In(PR_3)_2]^+ \overset{+PR_3}{\rightleftharpoons} \left([I_2In(PR_3)_3]^+\right)^{\ddagger} \overset{-PR_3}{\rightleftharpoons} [I_2In(PR_3)_2]^+$$

Dissociative:

$$[I_2In(PR_3)_2]^+ \overset{+PR_3}{\rightleftharpoons} [I_2In(PR_3)]^+ + 2PR_3 \overset{-PR_3}{\rightleftharpoons} [I_2In(PR_3)_2]^+$$

In view of the electron deficient nature of the $[InI_2]^+$ moiety the dissociative mechanism in which this species loses one of its stabilising ligands seems unlikely. Further evidence against this mechanism comes from the ^{31}P-n.m.r. spectra. If this dissociation was occurring in solution to any great extent then at low temperatures the spectra of the complex would exhibit a second signal corresponding to the unbound phosphine (provided that the rate at which the equilibrium occurs

slows to less than the n.m.r. time scale). The spectra shown in Diagram 8 show that this does not appear to be the case. This leaves the associative mechanism as the most likely to be occurring in solution. The apparently unfavourable steric crowding that would occur in the five co-ordinate intermediate for this process could be alleviated by an increase in In-P bond length.

^{115}In-N.m.r. spectroscopy has previously been shown to be useful for the identification of symmetrical species in solution such as the $[InX_4]^-$ anions (X=halide). For less symmetrical species, however, the signals are often so broad that they cannot be observed. An example of this is the compound $MeInI_2$ which in solution is believed to be ionic, $[Me_2InI_2][InI_4]$. The cation of this compound does not give a detectable ^{115}In-n.m.r. resonance, however, the symmetrical anion gives a signal in the expected position for $[InI_4]^-$.[54]

The ^{115}In-n.m.r. spectra of the series of 1:1 phosphine adducts of indium triiodide were obtained. The complexes with $HPBu^t_2$, $HPCy_2$ and PBu^i_3 all gave signals which are summarised in Table 4. For the complex with $HPPh_2$ no signal could be observed.

Table 4. ^{115}In-N.m.r. Data of indium triiodide phosphine complexes.

Complex	δ (ppm).	$\Delta\nu_{1/2}$ (Hz)
$InI_3.HPBu^t_2$	-228	3800
$InI_3.PBu^i_3$	-94	3400
$InI_3.HPCy_2$	-185	6100

Relative to $[In(H_2O)_6]^{3+}$ (0.5 mol dm^{-3}) in D_2O. The spectra were recorded on $CDCl_3$ solutions.

The fact that signals could be observed for these complexes is strongly indicative of the presence of a highly symmetrical species in solution such as the $[InI_4]^-$ anion. As mentioned above, no signal would be expected for species of the type InX_2L_2. The $[InI_4]^-$ anion has been shown to have a chemical shift of approximately -570 ppm relative to $[In(H_2O)_6]^{3+}$, which is somewhat shifted from the signals observed in the spectra of these complexes.[54] The half-height line widths observed for these signals are also greater than would be expected for the $[InI_4]^-$ anion (normally *ca.* 1000Hz in CD_2Cl_2). It has been shown, however, that for $[InCl_4]^-$ anions changing the solvent from CD_2Cl_2 to $CDCl_3$ more than doubles the width of the observed ^{115}In-n.m.r. resonance.[54] If the same effect occurs for the $[InI_4]^-$ anion on changing solvents then the half height line widths observed in this experiment would be closer to the expected values. Any further line broadening and the disparity in chemical shifts can be accounted for if there exists in solution an equilibrium between the ionic form of these complexes and the covalent tetrahedral form. In that case the signals would be shifted to a time-averaged position.

$$2InI_3.PR_3 \rightleftharpoons [InI_2(PR_3)_2]^+ + [InI_4]^-$$

The absence of a signal for the diphenylphosphine complex suggests that this compound does not dissociate into an ionic dimer and so does not form the $[InI_4]^-$ anion in solution. This ligand is the least basic of the phosphines whose complexes were studied using ^{115}In-n.m.r. spectroscopy and so it is likely that it is less capable than the other phosphines of stabilising the electron deficient $[InI_2]^+$ cation. Hence, the ^{115}In-n.m.r. spectrum shows that the $[InI_4]^-$ anion is not

present in solution. This is also consistent with the absence of ^{115}In coupling in the ^{31}P-n.m.r. spectrum of the diphenylphosphine complex. Such coupling is dependent upon the energies of the inner core electrons of the indium atoms. Clearly, changing from an ionic structure to a covalently bound monomer will affect these core electrons and so a difference in the degree of coupling observed would be expected.

In conclusion, then, these 1:1 complexes formed between indium triiodide and phosphines have monomeric covalent structures in the solid state. In solution they undergo rapid ligand exchange equilibria and they also appear to dissociate to some extent into ionic dimers. The degree of this dissociation seems to be dependent upon the strength of the phosphine ligand and its ability to stabilise the $[InI_2]^+$ cation.

Single-Crystal *X*-ray Diffraction Study of $InCl_3.(PMe_3)_2$.

The bis-trimethylphosphine complex of indium trichloride has previously been prepared and subjected to a powder *X*-ray diffraction study.[135] This showed the complex to be isomorphous with $AlCl_3(NMe_3)_2$, that is, a trigonal bipyramidal structure with axial trimethylphosphine groups.

This complex was prepared and subjected to a single crystal *X*-ray diffraction study which confirmed the trigonal bipyramidal structure previously suggested. The molecular structure that was determined is shown in Diagram 10. The full list of bond lengths and angles is given in Appendix B (page 186). The mean Cl-In-Cl bond angle is 120.0° and the P-In-P bond angle is 175.7° and so the axial ligands are slightly

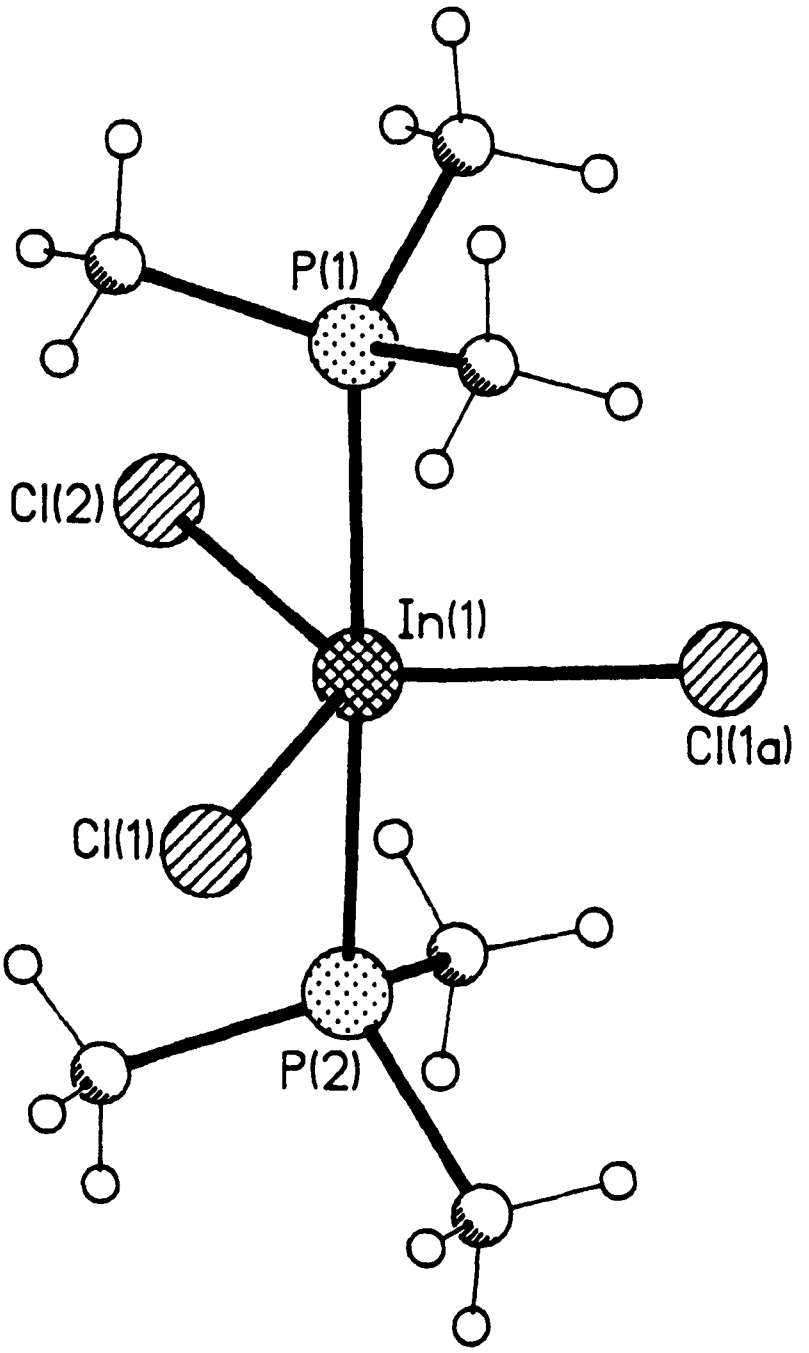


Diagram 10. View of the molecular structure of $InCl_3.(PMe_3)_2$ as determined by a single-crystal *X*-ray diffraction study. [Selected bond lengths (Å); In(1)-Cl(1), 2.505(3), In(1)-Cl(2), 2.450(4), In(1)-P(1), 2.575(3). Selected bond angles (°); Cl(1)-In(1)-Cl(2), 121.9(1), Cl(1)-In(1)-Cl(1a),116.1(1), P(1)-In(1)-P(2), 175.7(1).]

distorted from the ideal trigonal bipyramidal arrangement. The mean value of the In-P bond lengths is 2.58 Å which is in the range expected for In-P bonds. This value is discussed in relation to the other known In-P bond lengths in more detail in Appendix A (page 170). The mean value of the P-C bond lengths is 1.79 Å. This value is the same as the value found for the P-C bond length in $GaCl_3.PMe_3$.[130] The mean value of the In-Cl bond length is 2.49 Å. Previous workers [37] have estimated the normal indium-chlorine bond length as being 2.52 Å, which is only slightly longer than the In-Cl bond lengths found in this complex.

This structure can be compared to two similar structures that have previously been reported. The complex $InCl_3(PPh_3)_2$ has a mean In-Cl bond length of 2.38 Å and a mean In-P bond length of 2.71 Å.[38] The complex $InCl_3(NMe_3)_2$ has a mean In-Cl bond length of 2.37 Å.[39] The In-Cl bond length found in this study of $InCl_3(PMe_3)_2$ is approximately 0.1 Å longer than the values found for the other two structures and the In-P bonds are approximately 0.13 Å shorter than those in the analogous triphenylphosphine complex. This trimethylphosphine complex, therefore, has weaker equatorial interactions and stronger axial interactions than were found for the other two complexes. The apparently stronger interactions in this complex compared with those for the triphenylphosphine complex can be rationalised in terms of the electronic properties of the two phosphines. Trimethylphosphine is a much more basic ligand (pK_a=8.65) [133] than triphenylphosphine (pK_a=2.75) [133] and so would be expected to form a stronger donor bond. The weaker equatorial interactions in the trimethylphosphine complex are probably a consequence of the stronger axial interactions.

The bonding in these trigonal bipyramidal complexes has previously been described in terms of an sp^2 hybridisation of the metal

atom orbitals for the bonding with the equatorial chlorines leaving the vacant $5p_z$ orbital for bonding with the two axial phosphines. The possibility of the involvement of the vacant $5d_z2$ orbital in the bonding with the axial ligands (σ) has been discussed, but no firm conclusions were reached.[39] Thus, the apparent increase in In-P bond strength in $InCl_3(PMe_3)_2$ in comparison to $InCl_3(PPh_3)_2$ can also be rationalised in terms of an increased involvement of the indium $5d_z2$ orbital in the bonding with the axial ligands. The nature of this bonding is discussed in more detail in Appendix A (page 170).

Indium Triiodide Complexes of 1,2-Bis(diphenylphosphino)ethane.

While indium triiodide has been shown to form a 1:1 complex with diphos no spectroscopic data whatsoever have been reported for this compound and nothing is known about its structure.[20] Some complexes of the indium trihalides have been prepared with other bidentate ligands such as 1,10-phenanthroline. These complexes, however, were found to have a ligand : indium ratio of 1:1.5.[47] Studies of their vibrational spectra have lead to suggestions that they are ionic in the solid state with a structure of the type $[X_2InL_2][X_4InL]$, with each indium attaining octahedral co-ordination.

We have therefore studied the indium triiodide-diphos system in more detail and have found that not only could a 1:1 complex be prepared but also a 1:2 complex. Both of these complexes were prepared from acetonitrile solutions of indium triiodide and were isolated as colourless, moisture sensitive powders. Their identity was confirmed by

microanalyses (C,H,I). The infra-red spectra of these two complexes showed only slight differences and these are summarised in Table 5.

Table 5. Infra-red Data of the Diphos adducts.

Compound	Melt. Pt.	Infra red bands (cm^{-1})
$I_3In.Diphos$	140-144 °C	338(w),445(w),469(m),510(s),688(s), 720(s),740(m),770(w)840(w),876(w), 907(m),1023(m),1066(m),1092(s), 1105(s),1157(m),117(m),1275(m), 1303(m),1432(s),1569(w),1582(w).
$I_3In(Diphos)_2$	156-162 °C	342(w),435(w),470(m),481(m),510(s) 693(s),724(s),740(s),751(w),803(w), 920(w),1002(w),1026(m),1062(w), 1070(w),1095(m),1119(m),1150(m), 1187(m),1265(m),1308(m),1438(s), 1582(w).

In an attempt to obtain some structural information concerning these complexes some crystals of the 1:1 complex were grown. The majority of those obtained were needle-like in appearance and did not diffract *X*-rays. However, mixed in with these needles was a small quantity of well formed cubic crystals. These were found to diffract well and so a complete *X*-ray diffraction study was carried out on these. This showed that these crystals were in fact a 1:1.5 adduct, $(InI_3)_2(Diphos)_3$. The molecular structure of this compound is shown in Diagram 11. The bond lengths and angles for this structure are given in Appendix B (page 192). The structure of the complex shows that one molecule of diphos is bridging between the two indium triiodide molecules and also the unusual feature that the other two molecules of diphos are bonded through only one of their phosphorus atoms, the other remaining

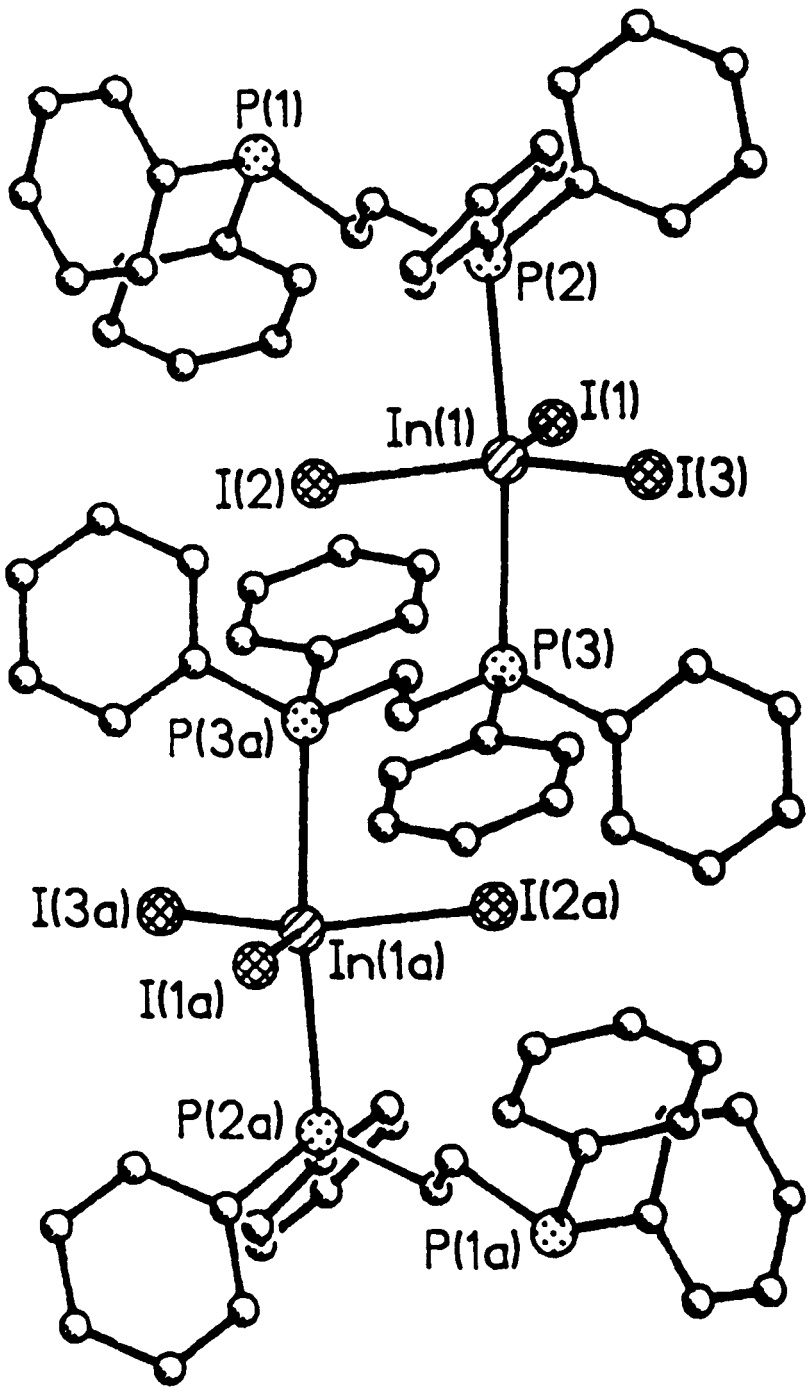


Diagram 11. Molecular structure of $(InI_3)_2(Diphos)_3$, as determined by a single-crystal *X*-ray diffraction study. [Selected bond lengths (Å); In(1)-I(1), 2.742(2), In(1)-I(2), 2.739(2), In(1)-I(3), 2.713(2), In(1)-P(2), 2.798(3), In(1)-P(3), 2.821(3). Selected bond angles (°); I(1)-In(1)-I(2), 119.7(1), I(1)-In(1)-I(3), 119.9(1), I(2)-In(1)-I(3), 120.4(1), P(2)-In(1)-P(3), 173.8(1).]

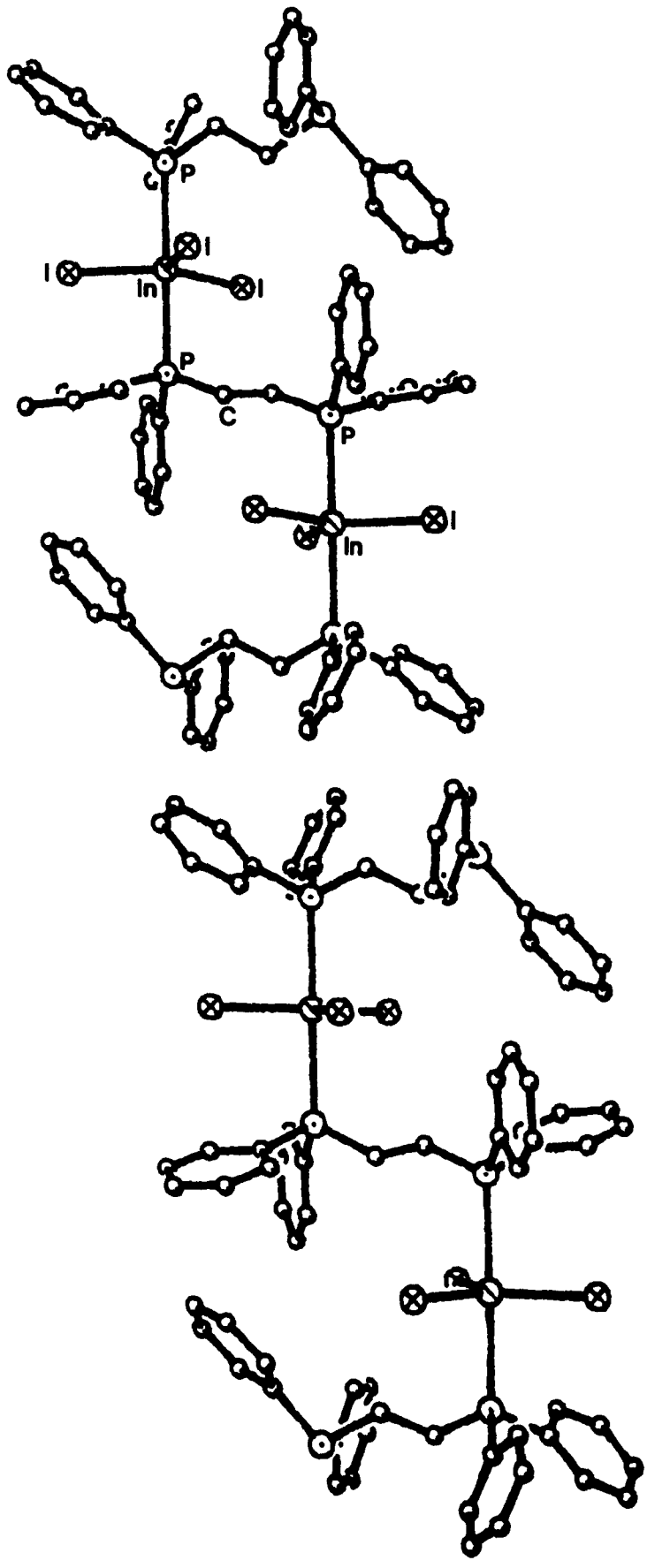
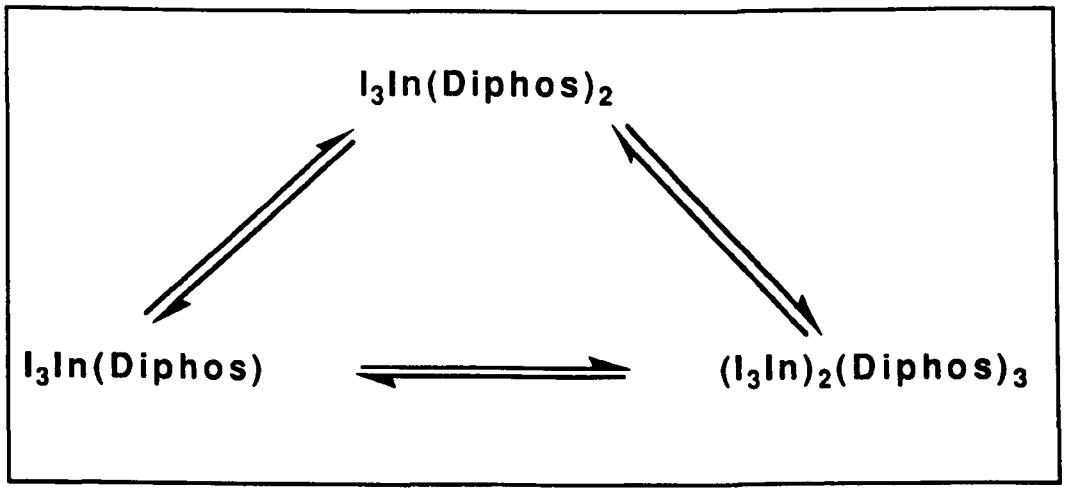


Diagram 12. View of two molecules of $(InI_3)_2(Diphos)_3$, showing the way in which they pack together in the crystal.

unco-ordinated. Each indium atom has an approximately trigonal-bipyramidal arrangement of the surrounding ligands. The mean value of the In-I bond lengths is 2.73 Å which is slightly longer than the values found in the tetrahedral phosphine complexes already described of 2.67 Å. This increase in length is consistent with an increase in the steric crowding around the indium on moving to a trigonal-bipyramidal from a tetrahedral geometry. The mean value of the In-P bond lengths is 2.81 Å. This is the longest In-P bond that has yet been reported. This bond length is discussed in relation to the other known In-P bond lengths in Appendix A (page 170).

This is the first example of a trigonal-bipyramidal structure that has been found for an indium triiodide complex. There are two surprising features about this structure that can be seen more clearly in Diagram 12. This shows the way in which two molecules of this complex are packed together in the crystal. Firstly there are no electronic interactions involving the unco-ordinated phosphorus atoms. Secondly the conformation of the molecules is such that there are unfavourable steric interactions between the phenyl rings. The conclusion to be reached from this is that the steric interactions between these phenyl groups must be only a minor factor in governing the conformation of the molecule. Other factors such as the packing arrangement within the crystal must be energetically more important.

Attempts at preparing this 1:1.5 complex free of other species proved to be unsuccessful. Taking indium triiodide and diphos in the correct ratio yielded a product which analysed as a mixture of 1:1.5 and 1:2 complexes. Recrystallisation of this mixture gave only the 1:2 complex. This fact taken in conjunction with the formation of a 1:1.5 complex from a solution of the 1:1 complex suggests that there exists in solution a facile equilibrium between the three species.



The $^{31}P\{^1H\}$-n.m.r. spectrum of the 1:2 and 1:1 complexes were obtained and showed only single resonances. This does not necessarily show that the phosphorus atoms in the diphos molecules are equivalent in these complexes, as rapid ligand exchange in solution would lead to a single, time averaged signal.

Nothing is known of the structures of the 1:1 and 1:2 complexes. Although there are several possibilities for each, both can take up trigonal-bipyramidal type structures based on that of the 1.5:1 complex. In the absence of further evidence, it seems reasonable to suggest that for these complexes the preferred structures are based on this. For these complexes the possible structures would then be as shown in Diagrams 13 and 14.

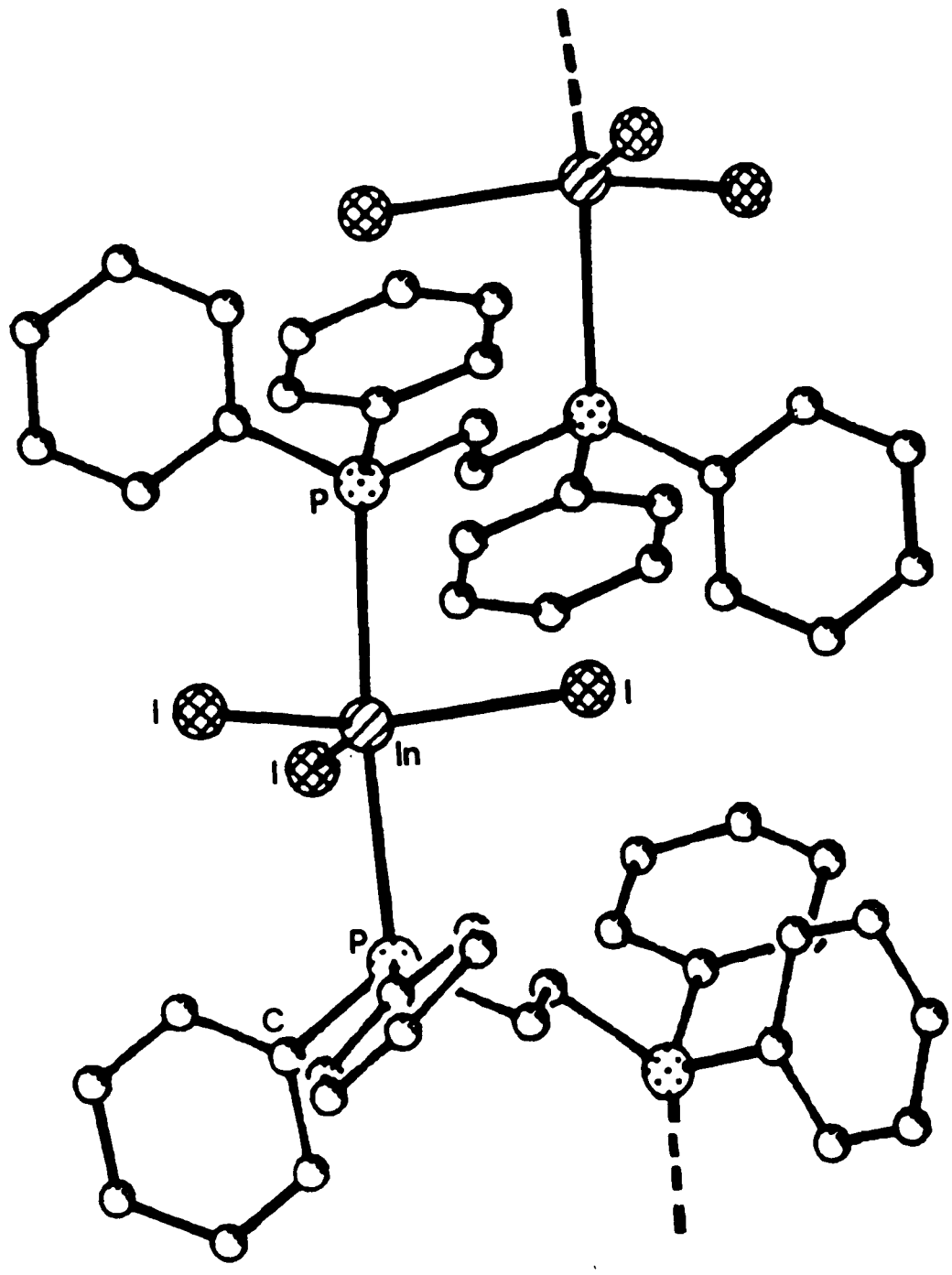


Diagram 13 Proposed structure of I_3In(Diphos).

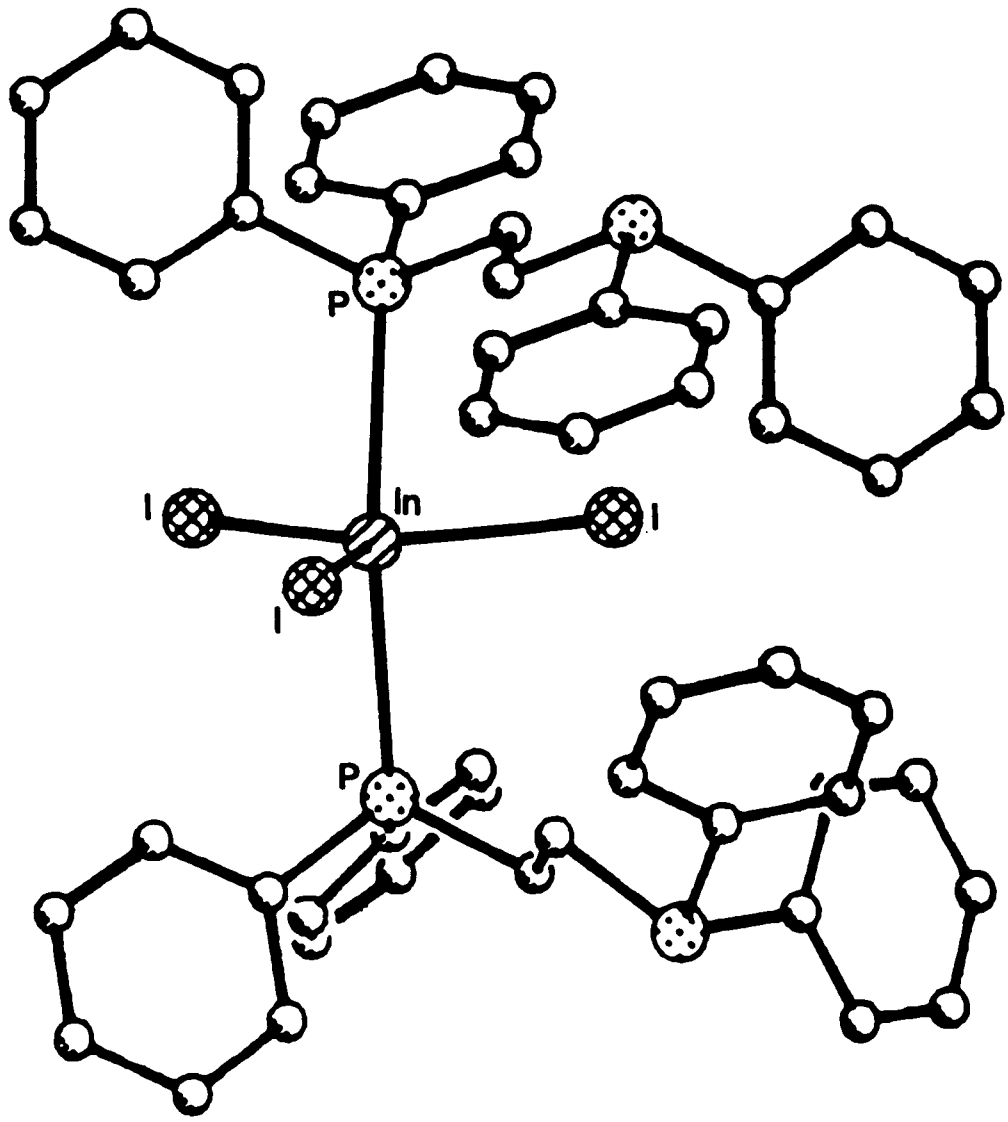
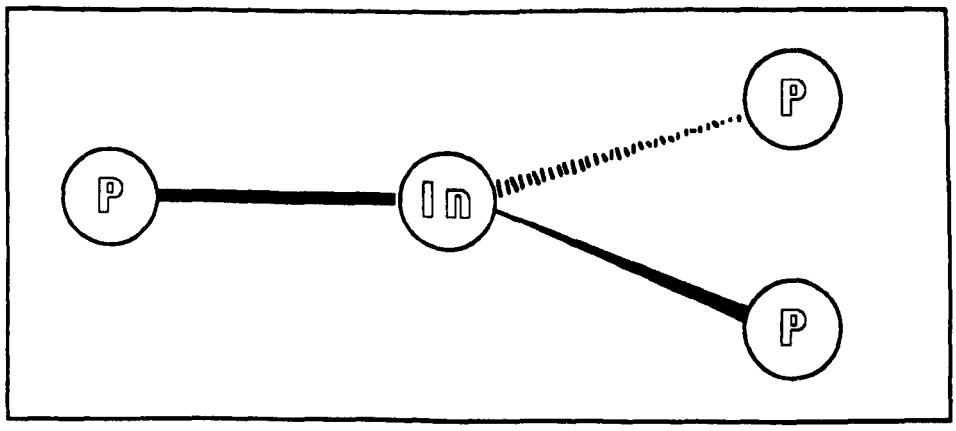


Diagram 14. Proposed structure of $I_3In(Diphos)_2$.

CHAPTER 3

METATHETICAL REACTIONS OF INDIUM HALIDES



Introduction.

It was mentioned in Chapter 1 that one of the requirements for the trimethylindium used in the MOVPE process is very high purity. This can be achieved by thermally "cracking" a trimethylindium-phosphine complex *in vacuo*. The normal method of preparation of these complexes is to prepare and isolate the trimethylindium and then to add the phosphine ligand to form the desired complex. The main drawback to this procedure is the extremely pyrophoric nature of the trimethyl indium. Once it is complexed to a phosphine it is much less air sensitive.

It was decided therefore that it would be of interest to investigate the possibility of preparing trimethylindium-phosphine complexes without isolating trimethylindium. The reaction scheme that was found to be most useful is the metathetical reaction between an indium trihalide-phosphine complex and methyllithium. It was mentioned in the introduction that indium trichloride will react with three equivalents of methyllithium to produce trimethylindium.[59] It was also pointed out that it has not been shown whether or not this reaction can be used with the other indium trihalides. It was therefore decided to investigate the reactions between methyllithium and some phosphine complexes of the indiumtrihalides (other than trichloride). For reasons of the ready availability of these complexes, this investigation has been concentrated on the indium triiodide complexes.

A second type of metathetical reaction of interest is that with phosphidolithium reagents. These can be reacted with the indium trihalides to introduce phosphorus containing groups. In the

introduction, the reaction between sterically congested phosphidolithium reagents and gallium trichloride was discussed. The reaction with (2,4,6-tri-*t*-butylphenyl)phosphidolithium in a 3:1 ratio is believed to produce a monomeric phosphido-gallium compound.[129] The corresponding reactions with the indium compounds are not known. Thus, it was decided to investigate the metathetical reactions of the indium trihalides with bulky phosphidolithium reagents.

Reactions of Indium Triiodide-Phosphine Complexes with Methyllithium.

During the course of this work it was found that the 1:1 complexes formed between indium triiodide and triphenylphosphine or di-*t*-butylphosphine react readily with one, two or three equivalents of methyllithium to yield the corresponding methylindium compounds and lithium iodide. These reactions were all carried out in toluene at room temperature. The reactions were found to proceed according to the following equations:-

$$I_3In.PR_3 + MeLi \longrightarrow MeInI_2.PR_3 + LiI$$

$$I_3In.PR_3 + 2MeLi \longrightarrow Me_2InI.PR_3 + 2LiI$$

$$I_3In.PR_3 + 3MeLi \longrightarrow Me_3In.PR_3 + 3LiI$$

$$(PR_3 = Bu^t{}_2PH;\ PPh_3)$$

The details of these reactions and their products are discussed below in two sections; one for the reactions with the triphenylphosphine complex and the other for the reactions with the di-*t*-butylphosphine complex.

Reactions of the Indium Triiodide-Triphenylphosphine Adduct with Methyllithium.

All three methylated compounds ($MeInI_2.L$, $Me_2InI.L$ and $Me_3In.L$; $L=PPh_3$) were prepared from the indium triiodide-triphenylphosphine adduct as toluene solutions. They were separated from the lithium iodide produced during the reaction by filtration. The colourless microcrystalline solids that precipitated from these solutions on cooling had to be recrystallised (with filtration) from boiling hexane to remove a small amount of lithium iodide that co-precipitated from the solution after the first filtration. The compounds were obtained in good yields (>70%) and were all moisture sensitive. They were identified by microanalyses (C,H,I,In) and ^{1}H-n.m.r. spectroscopy. Although $Me_2InI.PPh_3$ has previously been reported, its mass spectrum has not been reported and so this is discussed in more detail later.[59]

The ^{1}H-n.m.r. spectra of the three compounds are summarised in Table 1. The spectra all showed the expected signals with the correct integral ratios for 1:1 complexes of the predicted methylated compounds. The signals corresponding to the methyl groups show a regular up-field shift with increasing degree of methylation. This correlates with the replacement of the iodides with the less electronegative methyl groups.

Table 1. ^{1}H-N.m.r. Data of Methyl Derivatives of $I_3In.PPh_3$.

Compound	δ/ppm	Multiplicity	Integral Ratio	Assignment
$MeInI_2.PPh_3$ [a]	0.71	Singlet	3	In-C*H* $_3$
	7.57	Multiplet	15	PPh_3
$Me_2InI.PPh_3$ [a]	0.36	Singlet	6	In-C*H* $_3$
	7.52	Multiplet	15	PPh_3
$Me_3In.PPh_3$ [b]	0.07	Singlet	9	In-C*H* $_3$
	7.06, 7.43	Multiplets	15	PPh_3

[a]As $CDCl_3$ solution. [b]As d^8-toluene solution.

The infra-red spectrum of $Me_2InI.PPh_3$ has been previously reported [59] and showed three bands in the In-C stretching region at 515, 495 and 478 cm^{-1}. The infra-red spectrum of $MeInI_2.PPh_3$ obtained during the course of this work is very similar and also shows three bands in this region at 495, 503 and 520 cm^{-1}. Comparisons with the spectra of the analogous compounds with di-*t*-butylphosphine (discussed later) suggest that the band in the spectrum of $MeInI_2.PPh_3$ at 503 cm^{-1} can be tentatively assigned as an In-C stretching mode. Similarly the band at 496 cm^{-1} in the infra-red spectrum of $Me_2InI.PPh_3$ can be tentatively assigned as the $\nu_{asym}(InC_2)$ stretching mode.

The E.I. mass spectrum of $MeInI_2.PPh_3$ showed peaks corresponding only to triphenylphosphine (m/z=262) at low source

temperatures. Only as the source temperature increased (above ca. 150 °C) could peaks attributable to the compounds be seen. The molecular ion peak (plus a proton) (m/z=647) could be seen as well as peaks corresponding to sequential loss of the PPh_3 (m/z=384), an iodide (m/z=257) and a methyl group (m/z=242). These processes are represented in the following fragmentation scheme:-

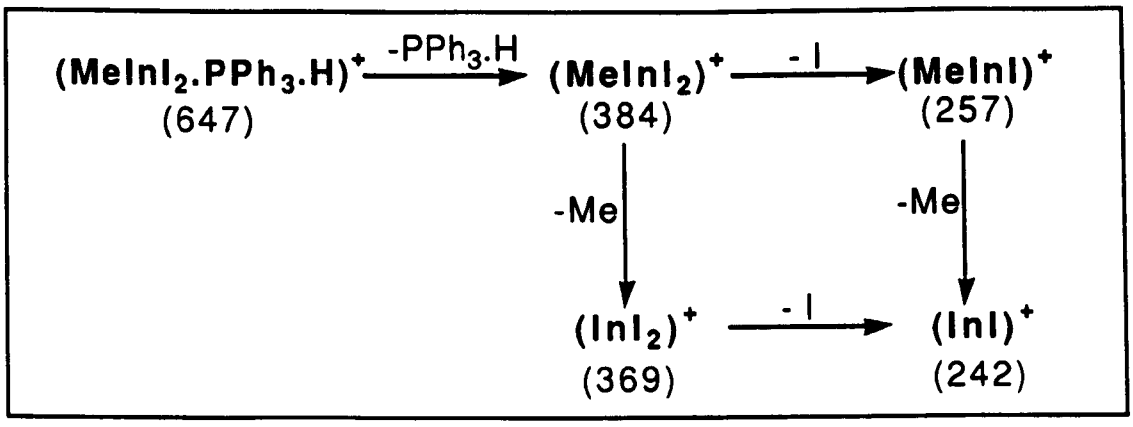


Diagram 1. Fragmentation scheme for mass spectrum of $MeInI_2.PPh_3$.

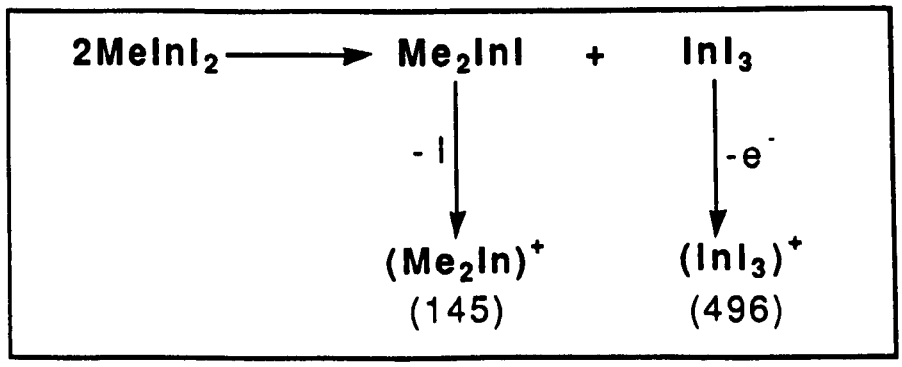


Diagram 2. Ligand exchange fragmentation scheme for mass spectrum of $MeInI_2.PPh_3$.

There were also peaks in the spectrum that corresponded to species produced by ligand exchange reactions. These are probably a result of the high temperatures required to volatilise the compound.

These side reactions gave rise to a peak corresponding to indium triiodide (m/z=496) as well as a peak corresponding to the $[Me_2In]^+$ cation (m/z=145). This is shown more clearly in the reaction and fragmentation scheme illustrated in Diagram 2.

From both of these reaction schemes it may be tentatively concluded that this complex is monomeric.

For $Me_2InI.PPh_3$ the chemical ionisation mass spectrum with ammonia produced the best results. Again the peaks corresponded to a monomeric molecular ion (plus two hydrogens) (m/z=536). Peaks could also be seen that correspond to fragments of this ion formed by sequential loss of the various groups bonded to the indium. This is best represented by the following fragmentation scheme:-

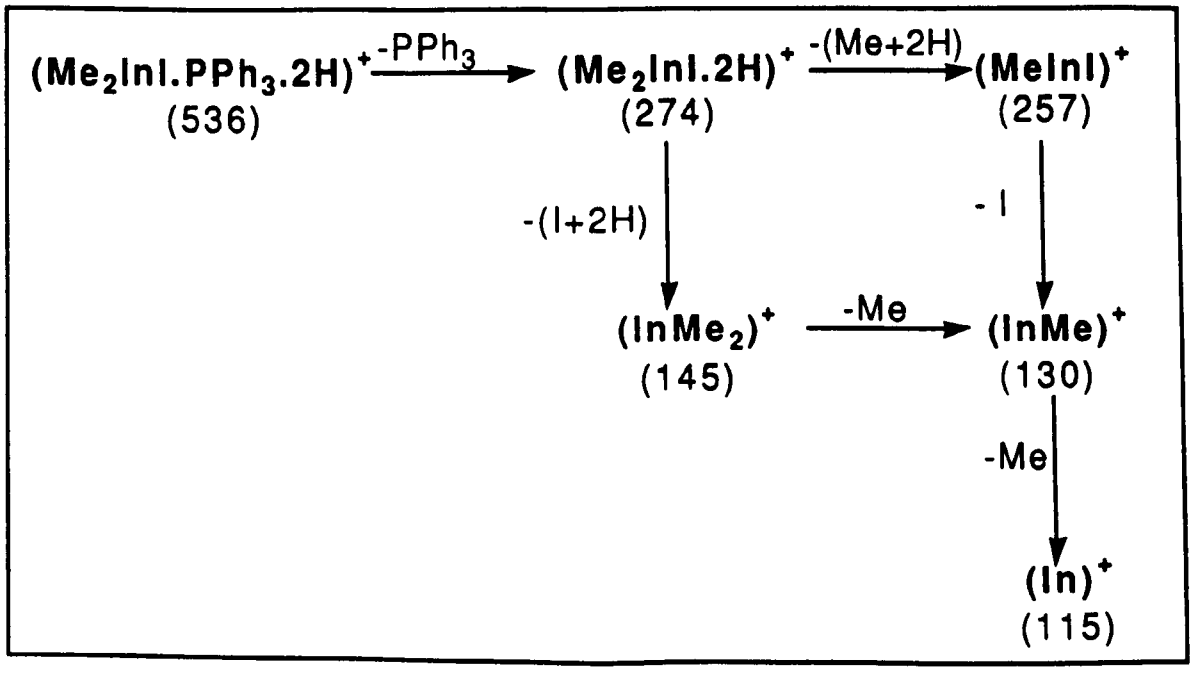


Diagram 3. Fragmentation scheme for mass spectrum of $Me_2InI.PPh_3$.

As was the case for $MeInI_2.PPh_3$, there are peaks in the mass spectrum of $Me_2InI.PPh_3$ corresponding to fragmentation of species produced from ligand rearrangement reactions. Thus, there is a peak corresponding to trimethylindium (m/z=162) and also an $[InI_2]^+$ cation (m/z=369). These are most probably produced according to the following scheme:-

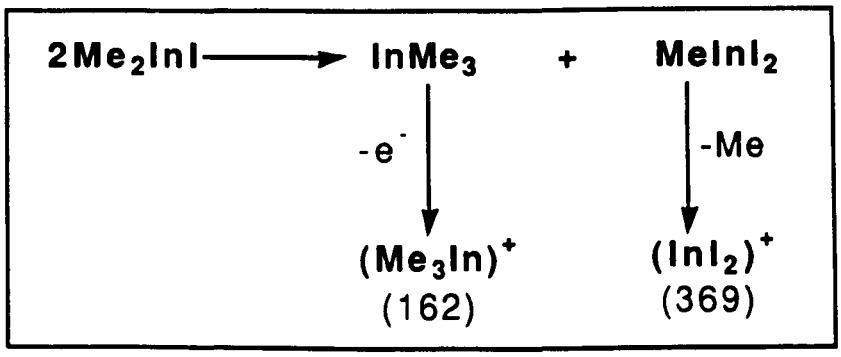


Diagram 4. Ligand Exchange Fragmentation Scheme for Mass Spectrum of $Me_2InI.PPh_3$.

It is conceivable that the $[InI_2]^+$ peak and the $[Me_3In]^+$ peak in this last scheme do not originate from the ligand redistribution reaction indicated. They could result from the fragmentation of $Me_2InI.PPh_3$ directly if this compound has an ionic structure of the type, $[I_2In(PPh_3)_2][InMe_4]$. This possibility, however, is eliminated by the infra-red spectrum of this compound. The compound $K[InMe_4]$ is known and its infra-red spectrum shows only one In-C stretching band at 465 cm^{-1}.[67] $Me_2InI.PPh_3$ does not contain a band corresponding to this $[InMe_4]^-$ anion in its infra-red spectrum and so it can be said conclusively that the compound does not contain this anion in the solid state. Having discounted this possibility, the two fragmentation

schemes proposed above are indicative of a monomeric four co-ordinate structure for this compound.

Reactions with Indium Triiodide-Di-*t*-butylphosphine Adduct.

All three of the methylated compounds ($MeInI_2$.L, Me_2InI.L and Me_3In.L; L=Bu^t_2PH) were prepared from the reaction of one, two or three equivalents of methyllithium at room temperature with a toluene solution of $I_3In.Bu^t_2PH$. The reactions were found to proceed via elimination of lithium iodide rather than the alternative possibility of deprotonation of Bu^t_2PH to give an anionic indium species (e.g. $Li[I_3InPBu^t_2]$). The solutions of $MeInI_2.Bu^t_2PH$ and $Me_2InI.Bu^t_2PH$ were filtered from the lithium iodide formed during the reaction. The solids that precipitated on cooling the solutions were recrystallised from a warm hexane/toluene mixture. The reaction mixture was never heated to more than 50°C to ensure that decomposition via methane elimination did not occur. The products were moisture sensitive, colourless solids which were identified by microanalyses (C,H,I,In) and their ^{1}H-n.m.r. spectra. (See Table 2).

The reaction with three equivalents of methyllithium gave a colourless solution after removal of the lithium iodide by filtration. The solvent (toluene) was removed from this under reduced pressure until there remained an oil. The ^{1}H-n.m.r. spectrum of this oil showed clearly that it was a mixture (approximately 1:1) of $Me_3In.HPBu^t_2$ and $Me_2InPBu^t_2$. The latter compound presumably is formed via methane elimination from $Me_3In.HPBu^t_2$. Heating this oil to 60°C caused the formation of a colourless air sensitive solid. This was recrystallised from

toluene to give a crystalline material. The ^{1}H-n.m.r. spectrum (see Table 2) and microanalysis for this compound showed that all of $Me_3In.HPBu^t_2$ had been converted into the phosphido derivative $Me_2InPBu^t_2$. The reaction with three equivalents of methyllithium, therefore, appears to proceed with the formation of the expected complex, $Me_3In.HPBu^t_2$, but this complex is then thermally unstable with respect to methane elimination and slowly gives the phosphido derivative.

$$I_3In.HPBu^t_2 + 3MeLi \longrightarrow Me_3In.HPBu^t_2 \xrightarrow{\Delta} Me_2InPBu^t_2$$
$$+ 3LiI \qquad + CH_4$$

An *X*-ray crystallographic study of $Me_2InPBu^t_2$ has recently been reported and shows it to be dimeric with two PBu^t_2 groups bridging between two indium atoms to give an In_2P_2 ring.[84]

The ^{1}H-n.m.r. spectra of the compounds that have been prepared are summarised in Table 2. The signals corresponding to the methyl groups show a similar up-field shift with increasing degree of methylation as was observed for the triphenylphosphine derivatives. The signal corresponding to the *t*-butyl groups in $(Me_2InPBu^t_2)_2$ appears as a triplet instead of the more usual doublet that might have been expected. This is a result of the dimeric nature of this compound in solution and is discussed later (see Chapter 4, page 131). $(Me_2InPBu^t_2)_2$ was found to be readily soluble in toluene and chloroform and was recrystallised from a hot toluene/hexane mixture. This is contrary to a recent report by Bradley *et al* [84] that this compound is completely

insoluble even in boiling toluene and hence they could not obtain the ^{1}H-n.m.r. spectrum of the compound. The ^{1}H-n.m.r. spectrum obtained in the work discussed here confirms that in our case the correct product was isolated.

Table 2. ^{1}H-N.m.r. Data of Methyl Derivatives of $I_3In.HPBu^t_2$.

Compound	δ/ppm	Multiplicity	Integral Ratio	Assignment
$MeInI_2.HPBu^t_2$ [a]	0.79	Singlet	3	In-C*H* $_3$
	1.05	Doublet	18	PBu^t_2
	3.76,5.27	Doublet	1	P-*H*
$Me_2InI.HPBu^t_2$ [b]	0.44	Singlet	6	In-C*H* $_3$
	1.06	Doublet	18	PBu^t_2
	2.66,4.03	Doublet	1	P-*H*
$Me_3In.HPBu^t_2$ [c]	-0.07	Singlet	9	In-C*H* $_3$
	0.74	Doublet	18	PBu^t_2
	2.43,3.68	Doublet	1	P-*H*
$(Me_2InPBu^t_2)_2$ [b]	0.24	Singlet	6	In-C*H* $_3$
	1.32	Triplet	18	PBu^t_2

[a]In $CDCl_3$. [b] In d^8-toluene solution. [c]In C_6D_6 solution.

Comparison of the methyl signals in ^{1}H-n.m.r. spectra obtained for these compounds with those already described for the triphenylphosphine analogues shows that no significant changes in chemical shift occur on changing the phosphine ligand. The largest difference is only 0.14 ppm for the difference between the methyl groups bonded to the indium in $Me_3In.PPh_3$ and $Me_3In.Bu^t_2PH$. This suggests that the structures of the compounds in solution do not change upon changing the phosphine ligand.

The infra-red spectra of these compounds exhibit bands that can be tentatively assigned as In-C stretches. The spectrum of $Me_2InI.HPBu^t_2$ shows two bands at 481 and 505 cm^{-1} which can be assigned by comparison with previous work [67] as $\nu_{sym}(InC_2)$ and $\nu_{asym}(InC_2)$ respectively. As has already been discussed for the triphenylphosphine analogue of this compound, the absence of an In-C stretch at 465 cm^{-1} indicates that this compound cannot be an ionic dimer in the solid state.[67] This leaves the four co-ordinate monomer as the most likely solid state structure. The infra-red spectrum of $MeInI_2.Bu^t_2PH$ exhibits only one band in the In-C range at 502 cm^{-1}. This compares well with the spectrum of $MeInI_2.PPh_3$ which also had only one band that could be assigned as an In-C stretch at 503 cm^{-1}. This indicates that the two compounds are likely to have the same basic structure, namely tetrahedral and monomeric. The phosphido derivative $(Me_2InPBu^t_2)_2$ exhibits two bands in the region for In-C stretches at 476 cm^{-1} and 503 cm^{-1} which can be tentatively assigned as $\nu_{sym}(InC_2)$ and $\nu_{asym}(InC_2)$ respectively. The infra-red spectrum of $Me_3In.Bu^t_2PH$ could not be obtained as this compound could not be isolated in the pure form.

The thermal stability of this series of adducts shows interesting behaviour. The observations made in capillaries in a melting point apparatus are summarised in Table 3.

Table 3. Thermal Stability of $InI_3.HPBu^t_2$ Derivatives.

Compound	Temperature(°C)	Observation.
$MeInI_2HPBu^t_2$	154-158	Melting point.
	above 158	Gas evolution occurred, eventually yielding a red/yellow tar.
$Me_2InIHPBu^t_2$	84-87	Melting point.
	87-180	Gas evolution
	180	Resolidified as a white solid.
	300	Turned into red tar.
$Me_3InHPBu^t_2$	—	Slowly evolved gas at room temperature. Rapidly at higher temperatures.

This behaviour can be rationalised in terms of reactions involving the acidic hydrogen atom of the phosphine ligand. For $MeInI_2.HPBu^t_2$ heating causes gas evolution and the formation of a reddish tar. This can be explained by the elimination of methane from the adduct according to the following equation:-

$$MeInI_2.HPBu^t_2 \xrightarrow{\Delta} 1/n(I_2InPBu^t_2)_n + CH_4$$

The red tar formed was not characterised but is likely to be a polymeric diiodophosphido indium compound. Attempts at preparing this compound by a metathetical reaction between $LiPBu^t_2$ and indium triiodide in a 1:1 ratio resulted in similar red intractable materials.

For $Me_2InI.HPBu^t_2$ gas evolution on heating eventually yields a white solid. This can also be explained in terms of methane elimination from the adduct, according to the following equation:-

$$Me_2InI.HPBu^t_2 \xrightarrow{\Delta} 1/n(Me(I)InPBu^t_2)_n + CH_4$$

A similar reaction to this has been reported for the preparation of $[Cl(Me)GaPEt_2]_n$ which was found to be a colourless polymeric solid.[87]

The E.I. mass spectrum of $MeInI_2.HPBu^t_2$ showed a molecular ion peak (plus one proton; m/z=531) and peaks resulting from sequential loss of Bu^t_2PH (m/z=384) and a methyl group (m/z=369) or an iodine atom (m/z=257). This can be seen clearly in the following fragmentation scheme:-

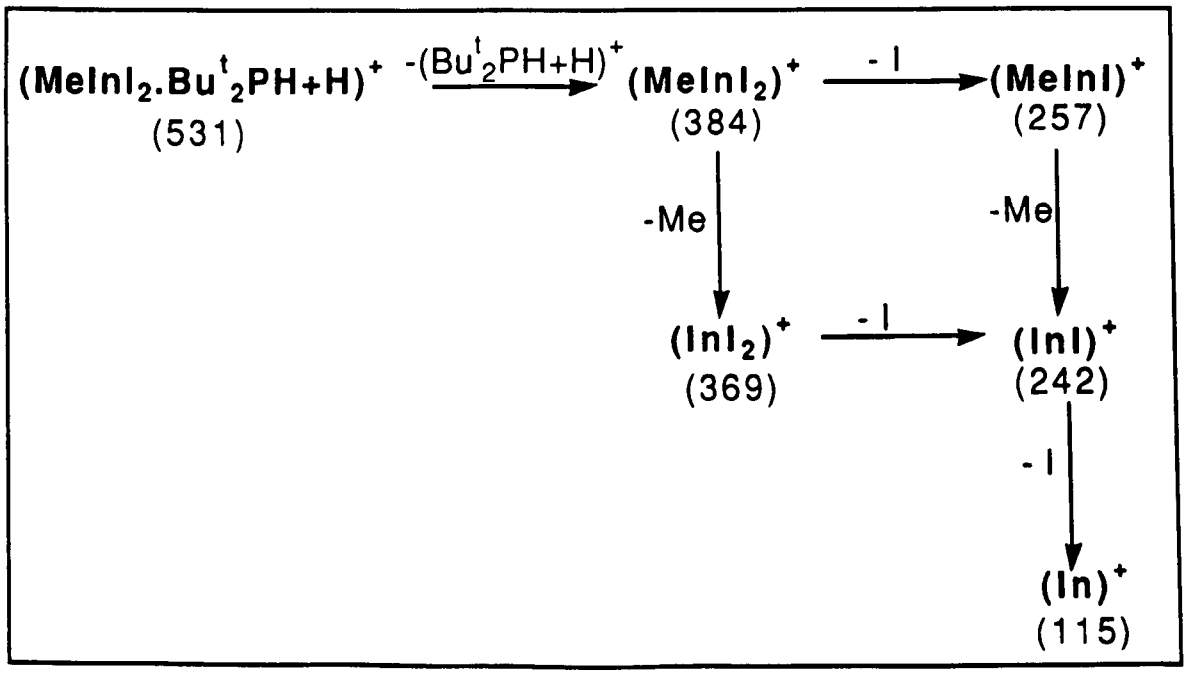


Diagram 5. Fragmentation scheme for mass spectrum of $MeInI_2.Bu^t_2PH$.

As was the case for the triphenylphosphine analogue of $MeInI_2.HPBu^t_2$, the high temperatures required to volatilise the compound sufficiently to obtain the mass spectrum caused a ligand exchange reaction to occur. Peaks in the mass spectrum corresponding

to $[InI_3]^+$ (m/z=496) and $[Me_2In]^+$ (m/z=145) are derived from this reaction.

$$2MeInI_2 \xrightarrow{\Delta} Me_2InI + InI_3$$

The E.I. mass spectrum of $Me_2InI.Bu^t{}_2PH$ showed a peak corresponding to the molecular ion (minus a hydrogen) (m/z=417), and sequential loss of either the methyl groups, the phosphine, or the iodides. There was also a peak corresponding to $[IInPBu^t{}_2]$ (m/z=387) which was presumably the result of methane elimination and loss of a methyl group from the molecular ion. This can be seen in the fragmentation scheme shown below:-

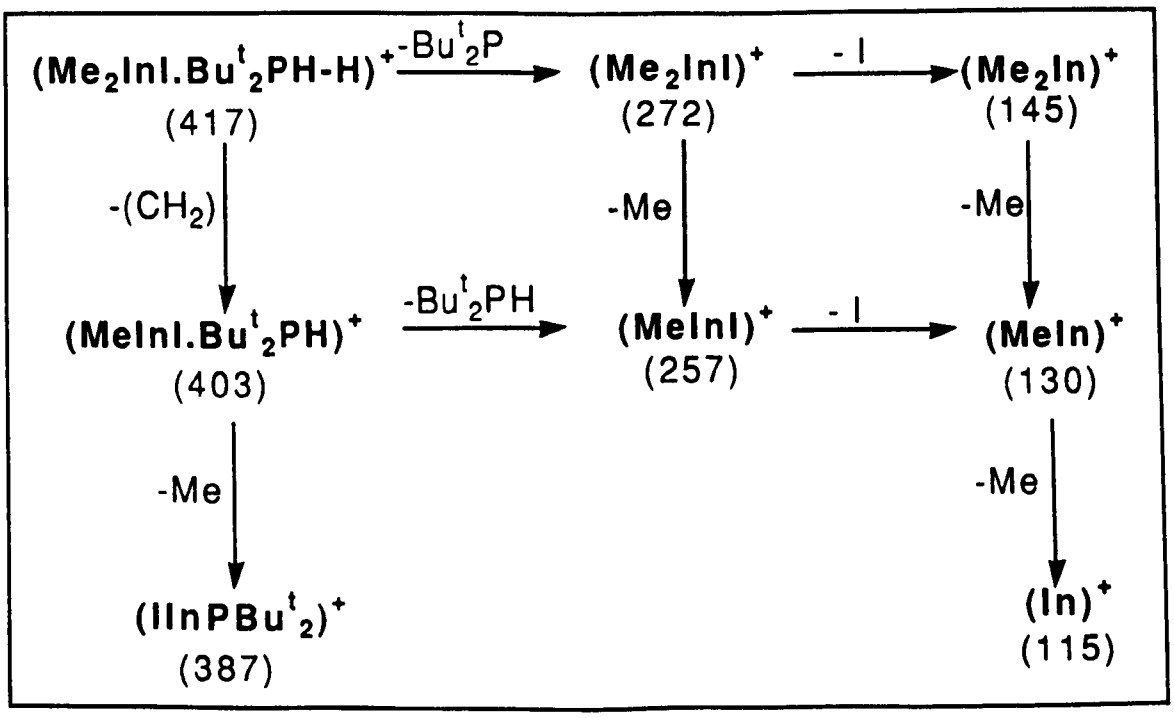


Diagram 6. Fragmentation Scheme for Mass Spectrum of $[Me_2InI.Bu^t{}_2PH]$.

The presence of a peak corresponding to an ion containing both a methyl group and in iodide [$(MeInI)^{+}$; m/z=257] suggests that the possible solid state structure of $[Me_2In(Bu^t_2PH)_2][InI_4]$ is unlikely as this could not easily give rise to such an ion). The mass spectrum also shows one peak which corresponds to the $[InI_2]^{+}$ ion (m/z=369). As is the case for the triphenylphosphine analogue, the likeliest source of this ion is fragmentation of $MeInI_2$, produced by a ligand exchange reaction.

$$2Me_2InI \xrightarrow{\Delta} InMe_3 + MeInI_2$$

The mass spectra of both $MeInI_2.Bu^t_2PH$ and $Me_2InI.Bu^t_2PH$ are indicative of a monomeric structure. No evidence was found in either spectrum for an ion corresponding to a dimeric structure. Such a structure would be unusual for complexes of the methylindium halides in view of the work that has been previously carried out on this area (see Chapter 1, page 35). Diagram 7 shows models of the probable structures of these two compounds.

Conclusions.

Indium triiodide complexes with phosphines will react in a stepwise manner with methyllithium eventually yielding the trimethylindium-phosphine adduct in yields of greater than 65%. This offers the possibility of a convenient method for preparing the organoindium adducts that are useful either as sources of pure trimethylindium (e.g. by cracking $Me_3In.PPh_3$ adduct) or as reagents in

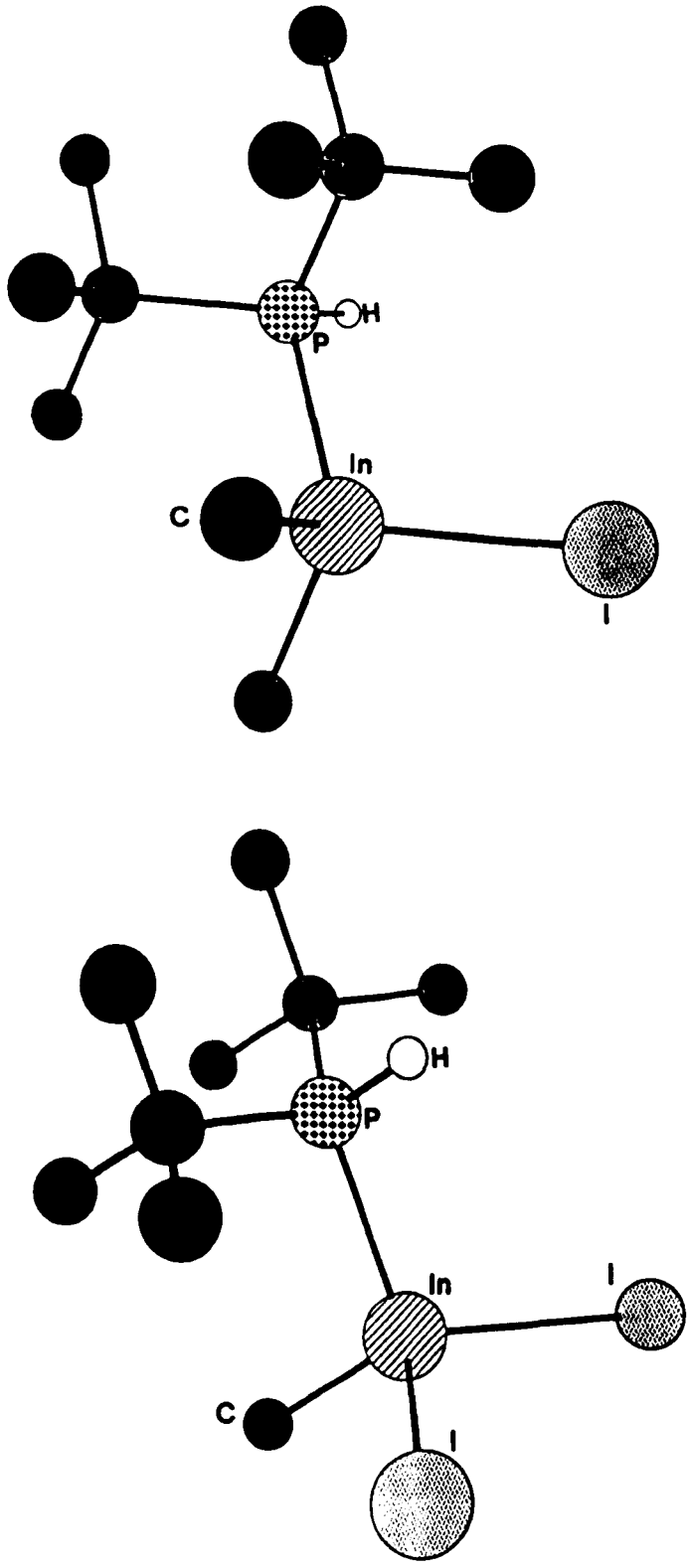


Diagram 7. View of models of the proposed structures of $Me_2InI.HPBu^t_2$ and $MeInI_2.HPBu^t_2$.

the preparation of indium phosphide. This method removes the need to isolate the pyrophoric trimethylindium and makes the desired compounds accessible from the much more stable indium trihalides.

Reactions of Indium Trihalides with Phosphidolithium Compounds.

The metathetical reaction between indium trichloride and lithium diphenylphosphide has been reported. The reactions with one, two and three equivalents of $LiPPh_2$ in diethylether, gave red intractable materials that could not be characterised. However, the reaction with four equivalents of the phosphidolithium compound resulted in the formation of an anionic indium species, according to the following equation[128]:-

$$InCl_3 + 4LiPPh_2 \xrightarrow{THF} [Li(THF)_4][In(PPh_2)_4] + 3LiCl$$

This ionic species was shown by an *X*-ray crystallographic study to be tetrahedral. A view of this structure is shown in Diagram 8. The polymeric species produced from the reaction of 1-3 equivalents of $LiPPh_2$ were probably the intermediate iodo-phosphido-indium species in which the likeliest cause of the polymerisation is In-P-In linkages.

This raises the question of whether or not monomeric, neutral phosphido-indium species can be prepared by this method. As has already been mentioned in the introduction, gallium trichloride has

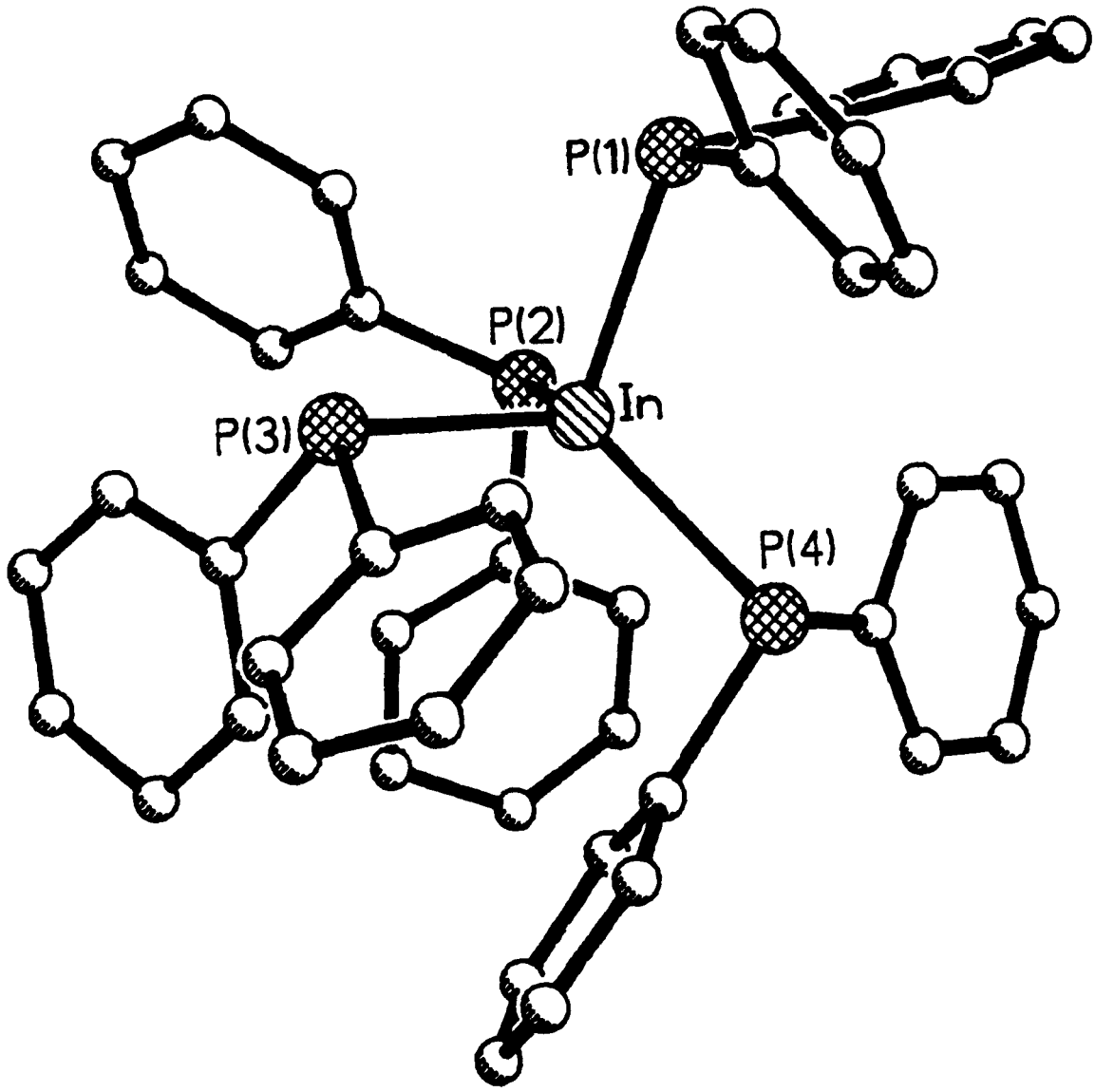


Diagram 8. View of the structure of the $[In(PPh_2)_4]^-$ anion.[128]

been shown to react with very sterically demanding phosphidolithium species to give trisphosphido compounds. These were thought to be monomeric, although a full *X*-ray crystallographic study was not possible.[129]

An investigation of the reactions between the indium trihalides and sterically hindered phosphidolithium compounds was therefore undertaken in an attempt to prepare a monomeric phosphidoindium compound.

Reaction of Indium Triiodide with Lithium Di-*t*-butylphosphide.

In the course of this work the reaction between indium triiodide and the sterically hindered phosphidolithium compound, $LiPBu^t_2$ was investigated. $LiPBu^t_2$ can most easily be prepared from the reaction between di-*t*-butylphosphine and *n*-butyllithium in hexane. The reaction mixture must be heated to *ca.* 60°C to effect the deprotonation reaction. The product readily precipitates in high yield on cooling the reaction mixture.

$$Bu^t_2PH + n\text{-}BuLi \xrightarrow{60°C} Bu^t_2PLi + n\text{-}BuH$$

The reactions with one or two equivalents of $LiPBu^t_2$ yielded red intractable materials which could not be identified. This was similar to the behaviour previously reported for the reaction with $LiPPh_2$.[128] The reaction with three equivalents of $LiPBu^t_2$ in toluene at room temperature produced dark grey suspensions that were presumed to be

the result of decomposition to indium metal. However, repeating this reaction with cooling to -78°C followed by slow warming to room temperature (typically over 30 minutes) produced a deep red solution and a pale coloured precipitate (LiI). The red solutution was removed from the precipitate by filtration, and after concentrating, cooling gave a crop of a bright red crystalline material that was extremely air sensitive. This product was identified by microanalysis (C,H,In) as the trisphosphido indium compound, $In(PBu^t_2)_3$.

$$InI_3 + 3LiPBu^t_2 \longrightarrow In(PBu^t_2)_3 + 3LiI$$

The ^1H-n.m.r. spectrum of this compound showed only one doublet at δ1.49ppm (doublet due to coupling to the phosphorus). The $^{31}P\{^1H\}$-n.m.r. spectrum also showed only one resonance at 71.8ppm. Both of these spectra show that in solution all of the *t*-butyl groups are equivalent, although, from this it cannot be said whether this is due simply to fluxionality or if it is due to a structural equivalence. The mass spectrum of this compound exhibited peaks that were derived only from a monomeric species. The chemical ionisation mass spectrum with ammonia showed a peak at m/z=568 which corresponds to the monomeric molecular ion plus ammonia. The E.I. mass spectrum showed a peak corresponding to loss of a methyl group from the molecular ion (m/z=532) and a peak corresponding to loss of a Bu^t_2P group (m/z=405). The peak corresponding to $[InPBu^t_2]^+$ (m/z=260) could also be seen. The most intense peaks in the E.I. mass spectrum were those deriving from the biphosphine, $Bu^t_2PPBu^t_2$. Thus, strong peaks could be seen that corresponded to $[Bu^t_2PPBu^t_2]^+$ (m/z=290), $[Bu^tPPBu^t_2]^+$ (m/z=233) and

$[Bu^tPPBu^t]^+$ (m/z=177). It would appear therefore that heating this compound in order to obtain its mass spectrum causes it to decompose according to the following equation:-

$$In(PBu^t_2)_3 \longrightarrow InPBu^t_2 + Bu^t_2PPBu^t_2 \longrightarrow \text{Further Fragmentation}$$

This reaction could also account for the thermal instability of the compound, which decomposes to a grey material at approximately 100°C. The intermediate "$InPBu^t_2$" indicated in the above equation is unknown and would most probably decompose rapidly to indium metal or possibly indium phosphide. This agrees with the observation of the formation of a grey material on heating.

All of the spectroscopic information discussed so far for this compound is consistent with but does not prove that the compound is monomeric. For this reason an *X*-ray crystallographic study of this compound was carried out. This confirmed the monomeric structure. Diagrams 9 and 10 show views of this structure. Three different molecules were located in the unit cell. The full list of bond lengths and angles is given in Appendix B (page 203).

The structure showed a trigonal planar InP_3 unit with a mean P-In-P bond angle of 120.0(5)° and a mean In-P bond length of 2.59 Å. This value is discussed in relation to the other In-P bond lengths that are known in Appendix A (page 170). The P-C bonds in this compound were found to have a mean length of 1.87 Å. This is identical to the mean P-C bond length found for $InI_3.Bu^t_2PH$ in Chapter 2 (page 61). Closer

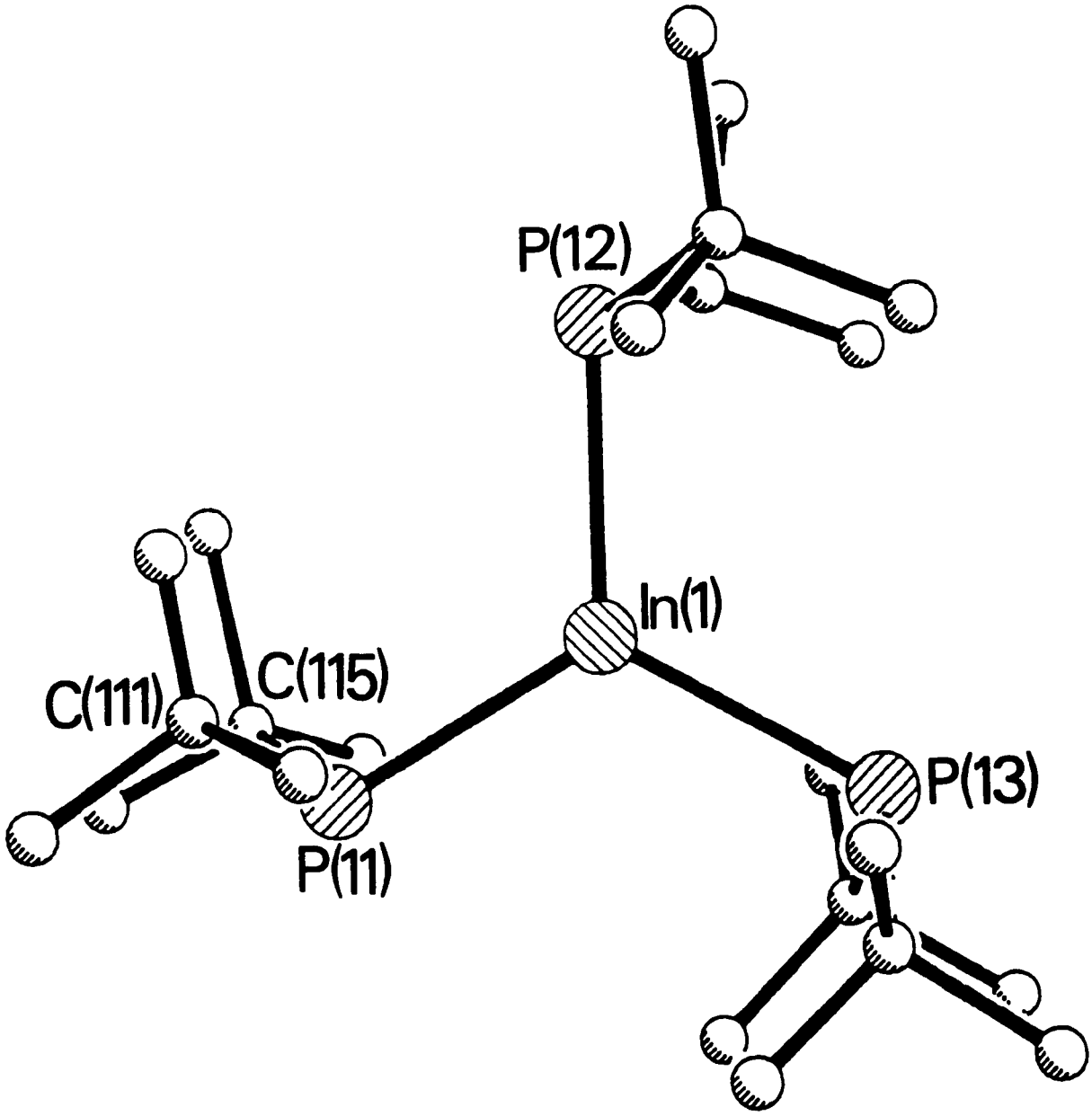


Diagram 9. View of the molecular structure of $In(PBu^t_2)_3$ showing the trigonal arrangement of the PBu^t_2 groups. [Selected bond lengths (Å); In(1)-P(11), 2.588(14), In(1)-P(12), 2.574(11), In(1)-P(13), 2.613(12). Selected bond angles (°); P(11)-In(1)-P(12), 120.7(4), P(11)-In(1)-P(13), 120.4(4), P(12)-In(1)-P(13), 118.8(4).]

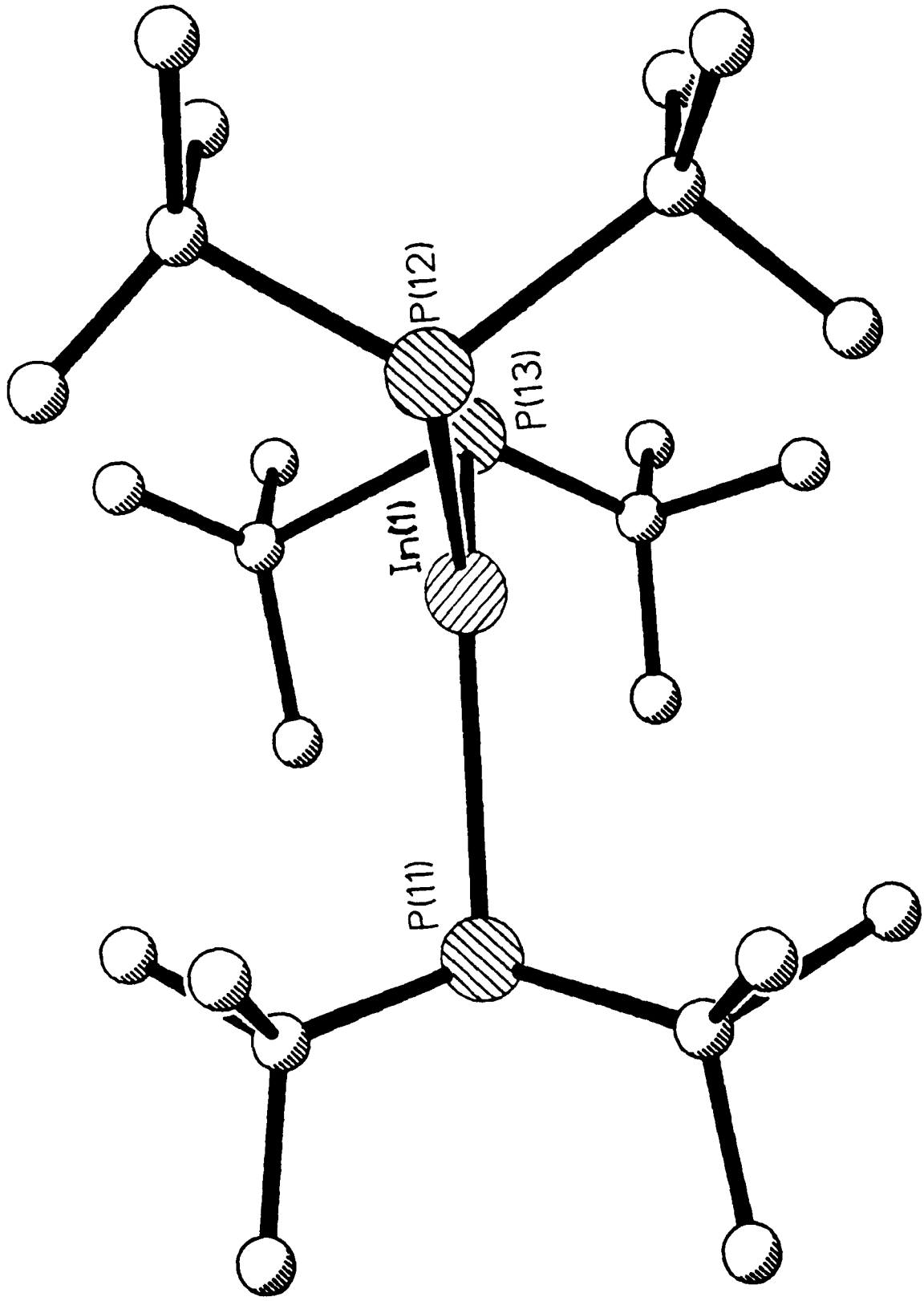


Diagram 10. View of the molecular structure of $In(PBu^t_2)_3$ showing the planar nature of the InP_3 unit.

inspection of the packing arrangement revealed that there were no axial interactions involving the vacant $5p_z$ indium orbital of any kind. This is, therefore, a genuine three co-ordinate indium compound. Diagram 11 shows a space filling model of this compound. The steric bulk of the *t*-butyl groups can be seen clearly. Their effect appears to be two fold. Firstly they hinder the metal centre so preventing any further substantial intermolecular interactions. Secondly, it can also be seen that they crowd the phosphorus atoms so making it unfavourable for them to co-ordinate to another indium centre. Attempts to co-ordinate a ligand to this compound (by adding THF, diethylether or triphenylphosphine) all failed. Even attempts to co-ordinate a sterically undemanding species such as a hydride (by reaction with sodium hydride in THF) were unsuccessful and left the $In(PBu^t_2)_3$ unchanged.

Several attempts were made at reacting $In(PBu^t_2)_3$ with acidic species in an effort to mimic the elimination reaction of indium trialkyls with such species. In each case the reaction proceeded to decomposition of the indium compounds. Clearly, the $In(PBu^t_2)_2$ fragment does not have the same degree of stability that is found for R_2In units. Even attempts at preparing compounds of the type $RIn(PBu^t_2)_2$ from the reaction of $LiPBu^t_2$ and RLi with indium trihalides were unsuccessful. An explanation for this could be that the decomposition reaction to form $Bu^t_2PPBu^t_2$ which has been observed in the mass spectrum of $In(PBu^t_2)_3$ and also on heating $(Et_2InPBu^t_2)_2$ (see Chapter 5) is very favourable for $RIn(PBu^t_2)_2$ type compounds. A possible mechanism for this decomposition reaction in relation to the structures of the compounds is discussed in Chapter 5.

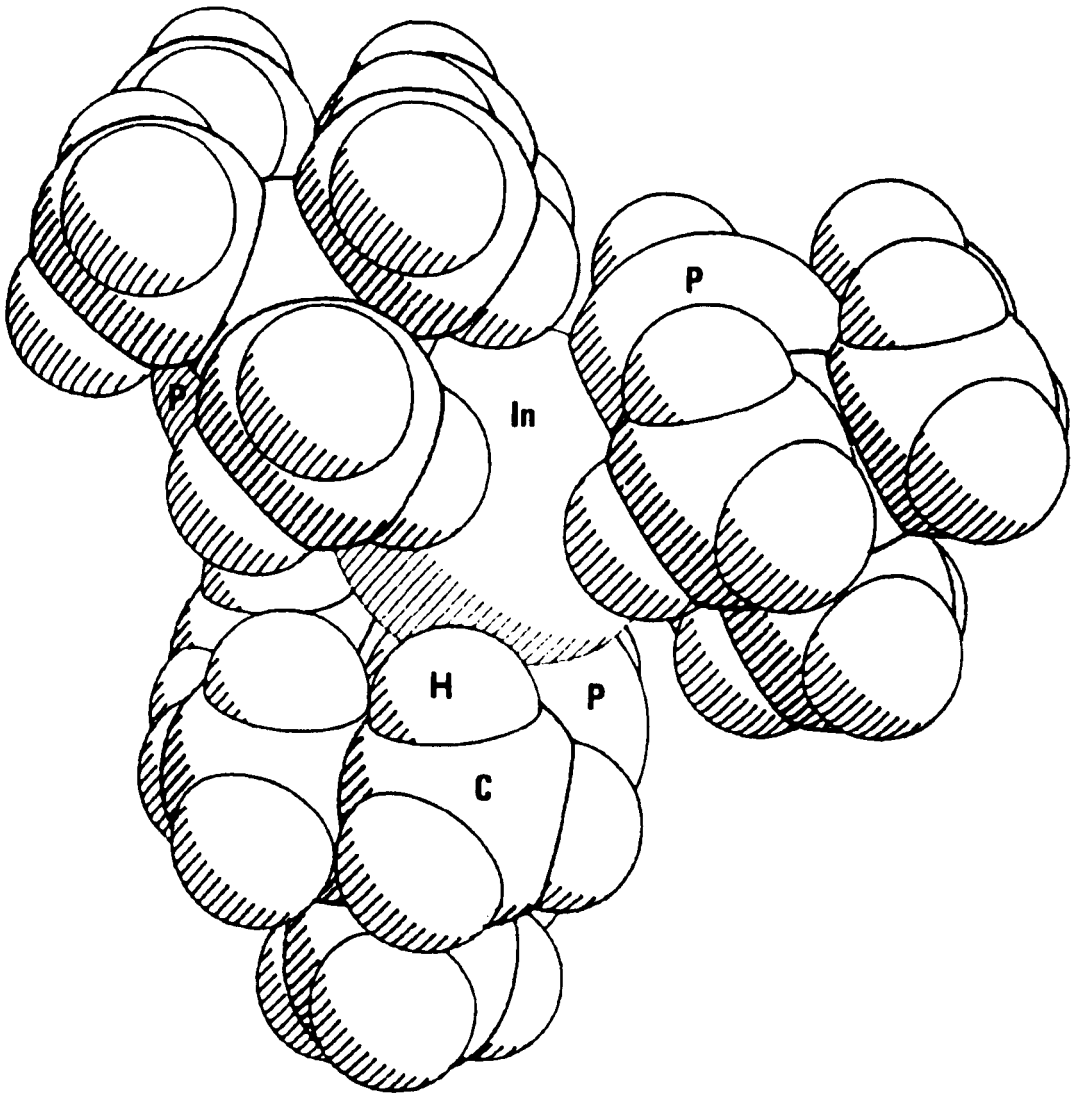


Diagram 11. View of a space filling model of $In(PBu^t_2)_3$ showing the sterically hindered indium and phosphorus atoms.

CHAPTER 4

REACTIONS OF TRIALKYL-INDIUM COMPOUNDS WITH SPECIES CONTAINING PROTONIC HYDROGENS

Introduction.

A discussion of the known reactions of organoindium compounds with compounds containing an active (protonic) hydrogen atom has already been given in Chapter 1. In the course of this work it was thought of interest to investigate some reactions of this type in an attempt to gain more information concerning not only the possible reactions but also the properties of the products.

One of the techniques that was used extensively in the characterisation of the compounds prepared during the course of this work was infra-red spectroscopy. The application of this technique in the study of organoindium chemistry is summarised below.

Infra-Red Spectra of Organoindium Compounds.

Common to the infra-red spectra of all organoindium compounds are In-C stretching vibrations. These bands are not only diagnostic of the presence of an In-C bond but can also be used to deduce information concerning bond angles (discussed below). The origin and frequency of these bands are therefore of interest to the work carried out in this study.

The infra-red spectrum of trimethyl indium vapour has been reported and shown to consist of three bands that can be assigned to In-C modes. This compound is monomeric in the vapour phase and the three bands occur at 500, 467 and 132 cm^{-1}.[136] The two at higher frequency are derived from stretching modes and the band at 132 cm^{-1} is derived from a deformation mode. These three modes are shown in Diagram 1.[30]

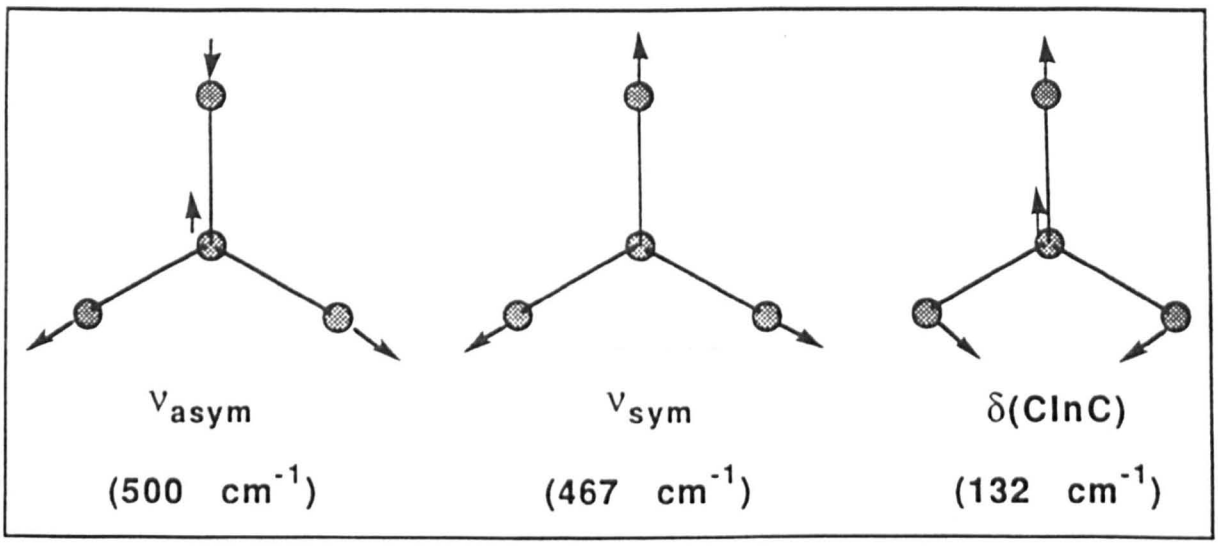


Diagram 1. In-C Vibrational modes of $InMe_3$ vapour .[30]

Replacing one of the methyl groups in this compound by another group (as in the reactions with compounds containing protonic hydrogen atoms) complicates the infra-red spectrum, in a manner which depends upon the nature of the new group. However, studies on a wide variety of compounds of general formula Me_2InX (where X represents any group) have shown that two stretching modes $\nu_{sym}(InC_2)$ and $\nu_{asym}(InC_2)$ are generally found at frequencies similar to the two stretching modes of $InMe_3$. These studies have led to bands in the range 460-490 cm^{-1} being assigned as $\nu_{sym}(InC_2)$ and bands in the range 480-560 cm^{-1} as $\nu_{asym}(InC_2)$.[84,86,111,137] It should, however, be noted that there are often several peaks in these regions arising from other vibrations, such as those from the third group bonded to the indium, and so exact assignments are not always possible. One potentially very useful trend in the positions of these two bands has been reported. Hausen *et al.*[67] have shown that there appears to exist a linear correlation between the frequency difference ($\Delta\nu$) between the symmetrical and antisymmetrical stretching frequencies and the C-In-C bond angle. This relationship is shown by a range of compounds some of

which are shown in Diagram 2. It should, therefore, be possible to predict the C-In-C bond angle from the infra-red spectrum of a compound provided that the bands for the pure InC_2 stretching frequencies can be correctly assigned.

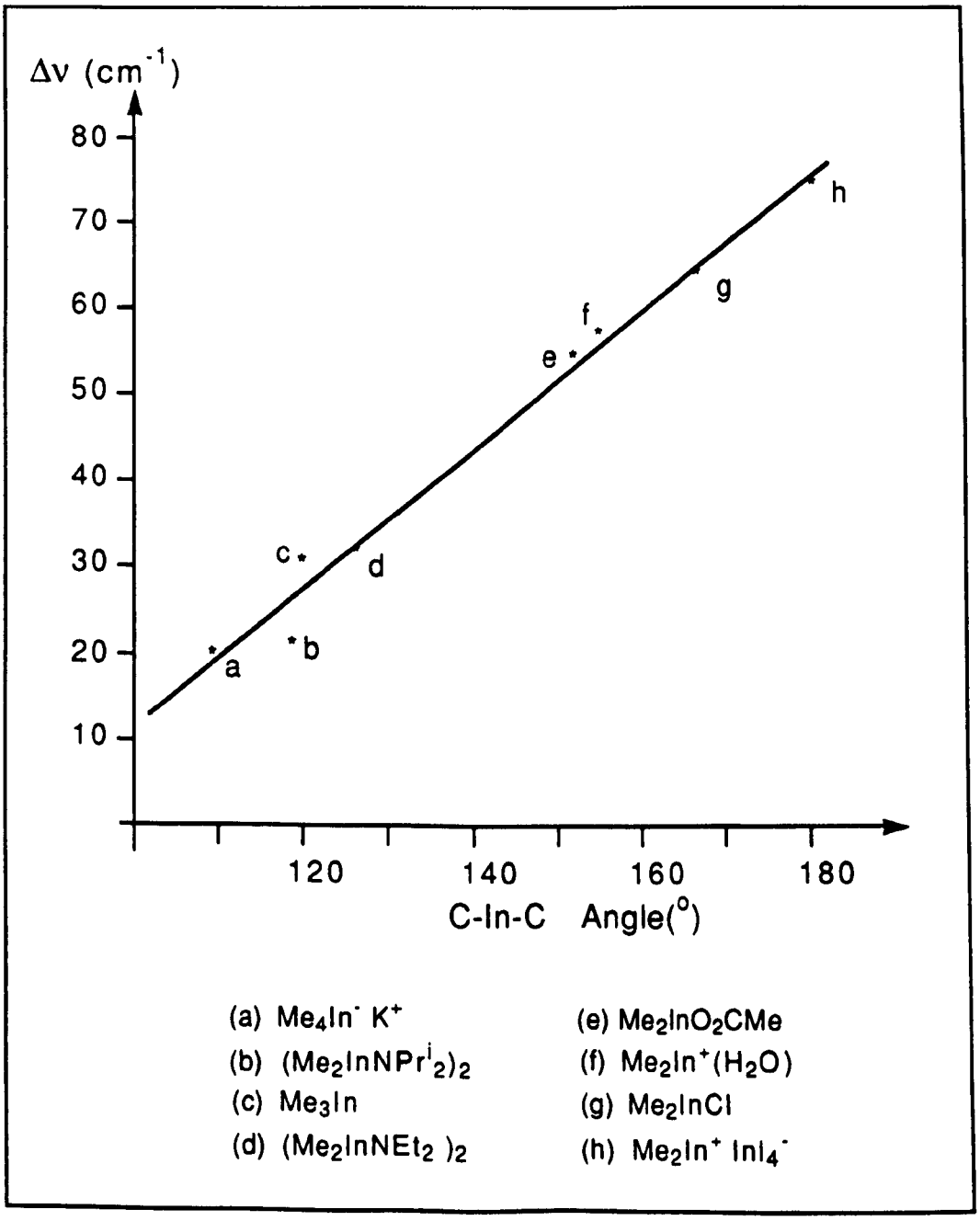
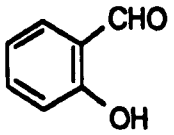
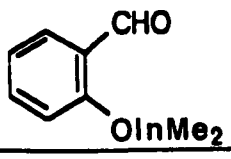
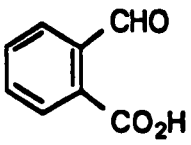
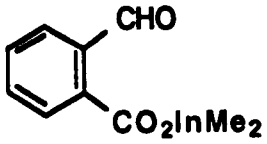
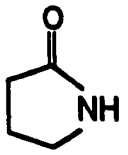
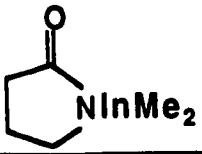
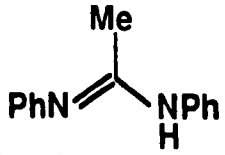
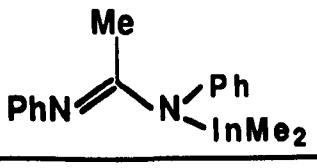


Diagram 2. Graph of the difference in frequency between the symmetrical and antisymmetrical stretching frequencies and the C-In-C bond angle for dialkyl indium species.[67]

Reactions of Trimethyl and Triethylindium with compounds Containing Protonic Hydrogens.

A range of novel organo-indium derivatives has been prepared by reaction of either trimethylindium or triethylindium with a range of compounds containing active protons.

Table 1. Reactions of Indium Trialkyls with Compounds Containing Protonic Hydrogens.

InR_3	Acid	React. temp.	Product
$InEt_3$	$HPBu^t_2$	70°C	$Et_2InPBu^t_2$
$InEt_3$	$HC{\equiv}CPh$	60°C	$Et_2InC{\equiv}CPh$
$InEt_3$	$H_2NCH_2CH_2OH$	25°C	$H_2NCH_2CH_2OInEt_2$
$InMe_3$		25°C	
$InMe_3$		25°C	
$InMe_3$		25°C	
$InMe_3$		25°C	

In most cases the elimination of alkane occurred at room temperature, however, in a few cases heating of the reaction mixture was necessary to effect elimination. The reactions that were carried out are summarised in Table 1. The gases evolved in these reactions were not identified, but were assumed by analogy with previous work[86] to be methane or ethane depending upon the starting materials.

The triethylindium used in these reactions was prepared by adapting the method of Todt and Dötzer [57] by refluxing ethylmagnesium bromide, bromoethane and indium metal together in diethylether. This reaction is believed to proceed in two stages. Firstly the bromoethane reacts with the indium metal to form the corresponding sesquihalide ($Et_3In_2Br_3$), and then this sesquihalide reacts with the ethylmagnesium bromide to give triethylindium. The triethylindium was obtained free of diethylether by fractional distillation from a mixture with benzene and its purity was confirmed by its ^{1}H-n.m.r. spectrum.

Trimethylindium for use in these reactions was prepared from methyllithium and indium trichloride in a 3:1 ratio in diethylether. The product was obtained by distillation and stored as an ether solution. Both of the trialkyls were stored and subsequently handled in a nitrogen-filled glove box.

Reaction of Triethylindium with Di-*t*-butylphosphine.

$$InEt_3 + Bu^t_2PH \longrightarrow Et_2InPBu^t_2 + C_2H_6$$

This reaction was found to occur readily on refluxing a 1:1 mixture of di-*t*-butylphosphine and triethylindium in hexane. On cooling the solution a colourless, air sensitive, crystalline solid

precipitated. This compound was identified by microanalysis (C,H,In) and its ^{1}H-n.m.r. spectrum (discussed in detail below). Attempts to carry out the reaction with two equivalents of phosphine gave the same products with the extra equivalent of phosphine remaining unreacted, even after refluxing in the higher boiling solvent toluene.

In order to determine the effect of the bulky PBu^t_2 groups on the structure of this compound, the solid state structure was determined by an *X*-ray crystallographic study. This showed the compound to be dimeric with bridging di-*t*-butylphosphido groups (see Diagrams 3 and 4). The In_2P_2 ring in this dimer was found to be almost planar. The In-P bond in this compound has a length of 2.635(2) Å. This compares well with the other known In-P bond lengths and is discussed in more detail in Appendix A (page 170). The mean value of the In-C bond lengths is 2.17(1) Å which falls within the expected range of 2.05-2.25 Å found in previous studies.[56,65,71,77,139] The dimerisation of this compound is in contrast to the trimerisation (in solution) that has been reported for analogous compounds with the less sterically hindered dimethyl- and diethylphosphido substituents.[86,87] This difference is presumably a result of the increased steric congestion that would occur around the six membered ring on changing from PMe_2 or PEt_2 groups to PBu^t_2 groups.

The four membered In_2P_2 ring that is found for this compound has internal angles of 85.6 and 94.4°. These are significantly less than the optimum value of 109.5° for atoms with a tetrahedral geometry. The fact that this dimeric structure is the one that is found suggests that the steric crowding that would occur between the *t*-butyl groups in the alternative trimeric structure is less energetically favourable than the ring strain introduced in the four membered ring of the dimer.

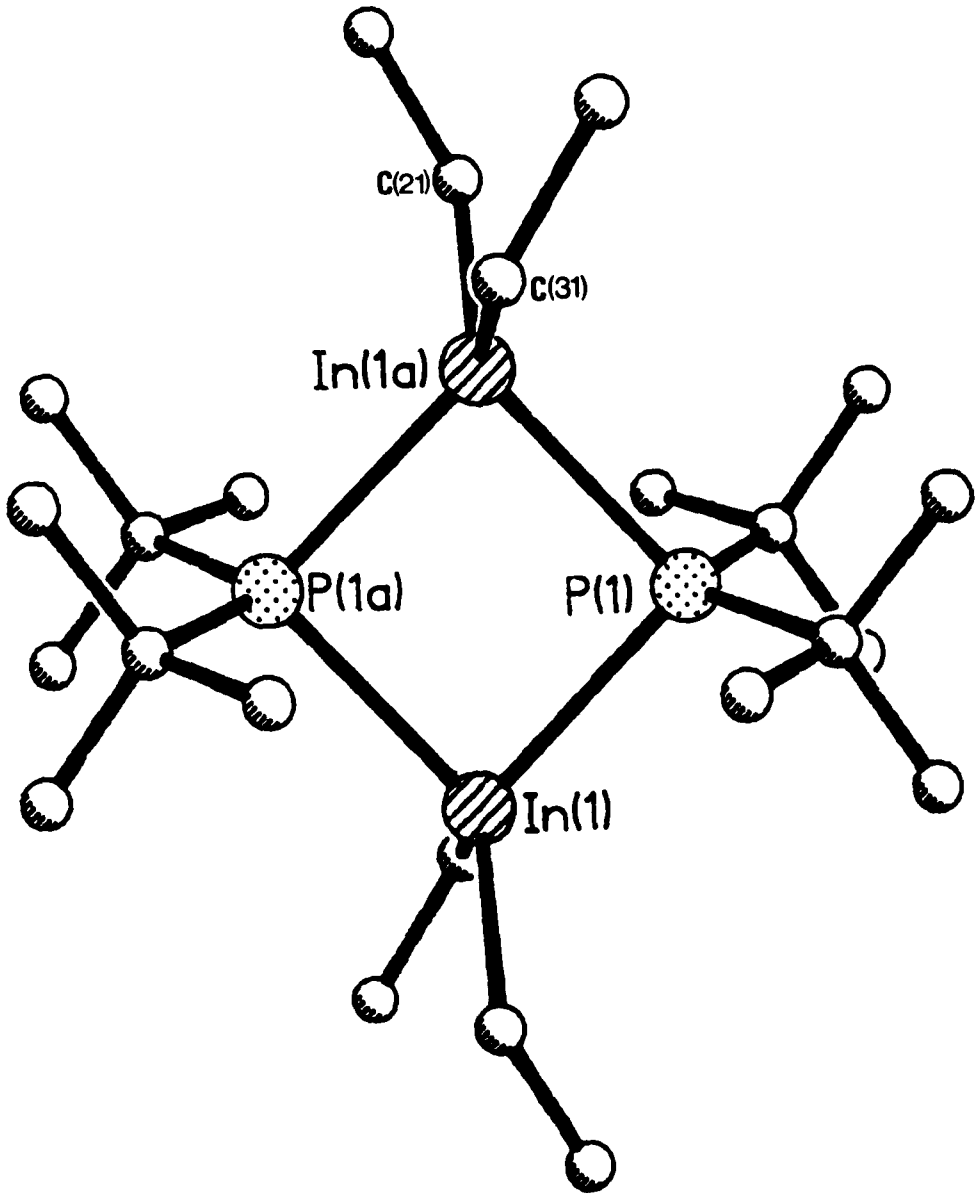


Diagram 3. View of the molecular structure of $(Et_2InPBu^t_2)_2$ as determined by a single-crystal *X* -ray crystallographic study. [Selected bond lengths (Å); In-P(1), 2.635(2), In-C(21), 2.170(13), In-C(31), 2.176(12), P(1)-C(1), 1.879(8). Selected bond angles (°); In-P(1)-In, 94.4(1), P(1)-In-P(1'), 85.6(1), C(31)-In-C(21), 113.5(5)]

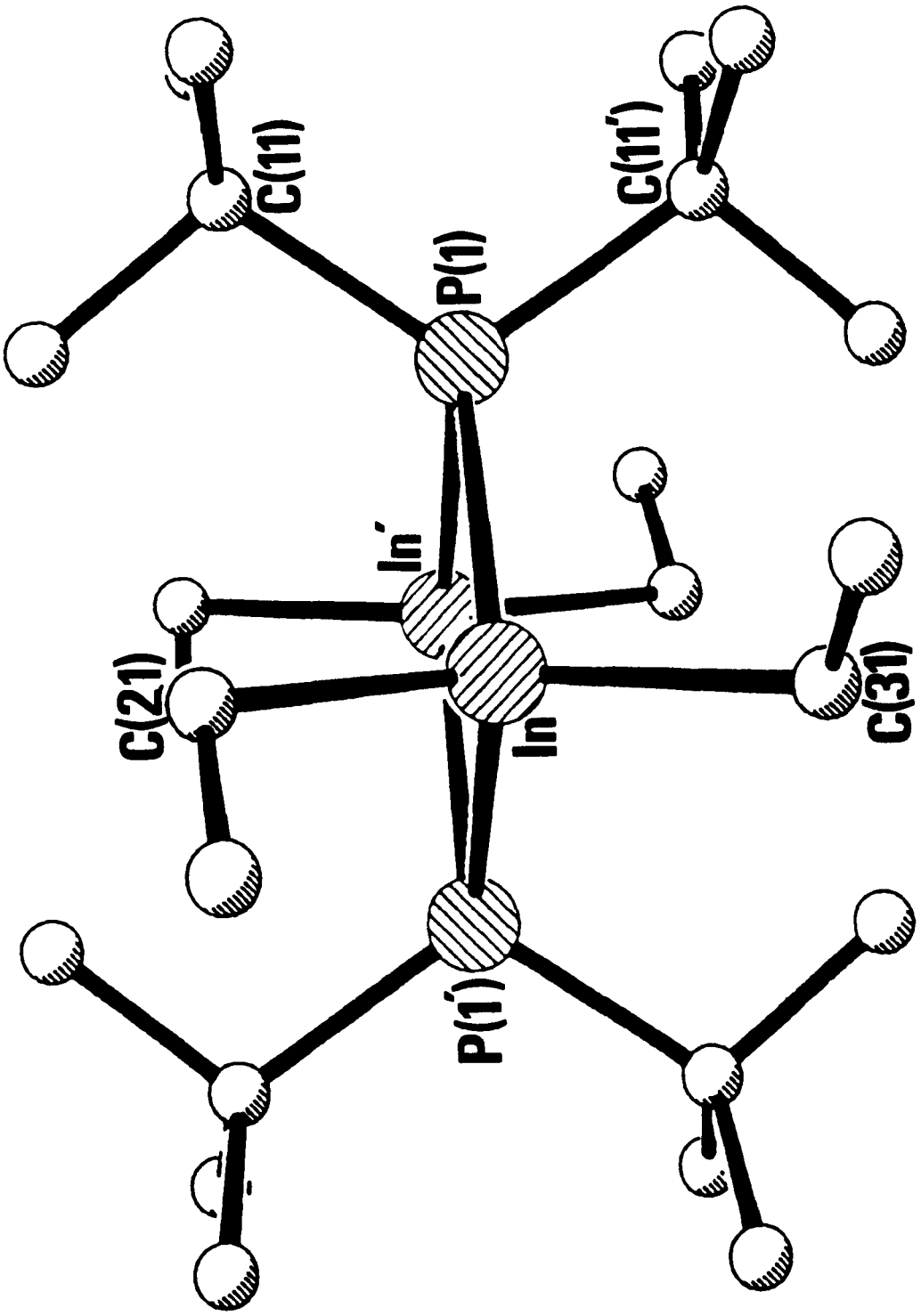


Diagram 4. View of the molecular structure of $(Et_2InPBu^t_2)_2$ showing the planar nature of the In_2P_2 ring.

A compound similar to this has been reported since this work was completed, $(Me_2InPBu^t_2)_2$, has been shown to have the same dimeric structure as its ethyl analogue, containing a planar In_2P_2 ring.[84] The important bond lengths and angles of the two compounds are compared in Table 2. The two structures compare very well and the size and internal angles of the two In_2P_2 rings are very similar. The small differences that are observed are probably due to the slightly different steric and electronic properties of the ethyl and methyl groups.

Table 2. Comparison of the bond lengths and angles found for the di-*t*-butylphosphine derivatives of trimethyl- and triethylindium.

	$(Et_2InPBu^t_2)_2$ [(a)]	$(Me_2InPBu^t_2)$ [(b)]
In-P (Å)	2.635	2.637 2.656
In--In(Å)	3.868	3.897
P-In-P(°)	85.6	85.2
In-P-In(°)	94.4	94.8

[(a)]This work. [(b)]From reference 84.

The mass spectrum of $(Et_2InPBu^t_2)_2$ is in good agreement with the solid state structure and shows peaks that can be assigned to both monomer and dimer fragmentation. The spectrum is summarised in Table 3. This confirms that the dimerisation is relatively strong and is not destroyed by the energy input required to obtain the mass spectrum.

Table 3. Summary of the E.I. Mass Spectrum of $(Et_2InPBu^t_2)_2$.

m\z	Assignment	m/z	Assignment
621	$(D\text{-}Me)^+$	433	$(D\text{-}2Et\text{-}PBu^t_2)^+$
579	$(D\text{-}Bu^t)^+$	319	$(M+H)^+$
491	$(D\text{-}PBu^t_2)^+$	289	$(M\text{-}Et)^+$
463	$(D\text{-}Et\text{-}PBu^t_2)^+$	173	$(Et_2In)^+$

The ^{1}H-n.m.r. spectrum of this compound showed the expected triplet and quartet for the ethyl groups. However, the signal arising from the *t*-butyl groups appeared as a 1:2:1 triplet with a coupling constant of approximately 7 Hz. Normally a doublet would be expected for these groups due to coupling to the phosphorus atom to which they are bound. As was mentioned earlier, the similar compound $(Me_2InPBu^t_2)_2$ also has a triplet in its ^{1}H-n.m.r. spectrum arising from its *t*-butyl groups. The explanation for this triplet lies in the structure of the compound. If the dimeric structure that is found in the solid state for both of these compounds is present in solution then the ^{1}H-n.m.r. would show coupling between the *t*-butyl group protons and the phosphorus atom to which these groups are attached. They would also show "strong coupling" to the other phosphorus atom in the In_2P_2 ring, further splitting the expected doublet into a 1:2:1 triplet. The fact that this triplet is observed in the ^{1}H-n.m.r. is consistent with the presence of the dimeric structure in solution.

The $^{31}P\{^{1}H\}$-n.m.r. spectrum of $(Et_2InPBu^t_2)_2$ shows only one signal at 44.8 ppm. This suggests that there is only one species present in solution. When this is considered in conjunction with the evidence of the ^{1}H-n.m.r. spectrum it may be concluded that the dimeric species persists in solution and does not dissociate into the monomer to any significant extent. If any of the monomer was present it would be expected to give rise to a second peak in the $^{31}P\{^{1}H\}$-n.m.r. spectrum (unless a rapid equilibrium between the two was occuring). Such a situation has been shown to occur for the related compound $[(Me_3SiCH_2)_2InPPh_2]_2$ for which the monomer-dimer equilibrium in solution occurs at a rate slower than the n.m.r. time scale and so signals corresponding to both species can be observed in its n.m.r. spectra.[55]

The infra-red spectrum (see Diagram 5) shows two bands in the In-C stretching range. A strong band at 463 cm^{-1} and a weak band at 529 cm^{-1} which can be tentatively assigned as the $\nu_{sym}(InC_2)$ and $\nu_{asym}(InC_2)$ stretching modes respectively. These assignments give a frequency difference of 66 cm^{-1}. If the relationship between this value and the C-In-C bond angle holds true then a bond angle in the region of 167° would be predicted. The actual value found in the crystal structure is 113.3°. This is quite a large discrepancy which may be a result of the presence of the bulky *t*-butyl groups causing molecular distortions not seen in the examples studied by Hausen *et al.*[67]

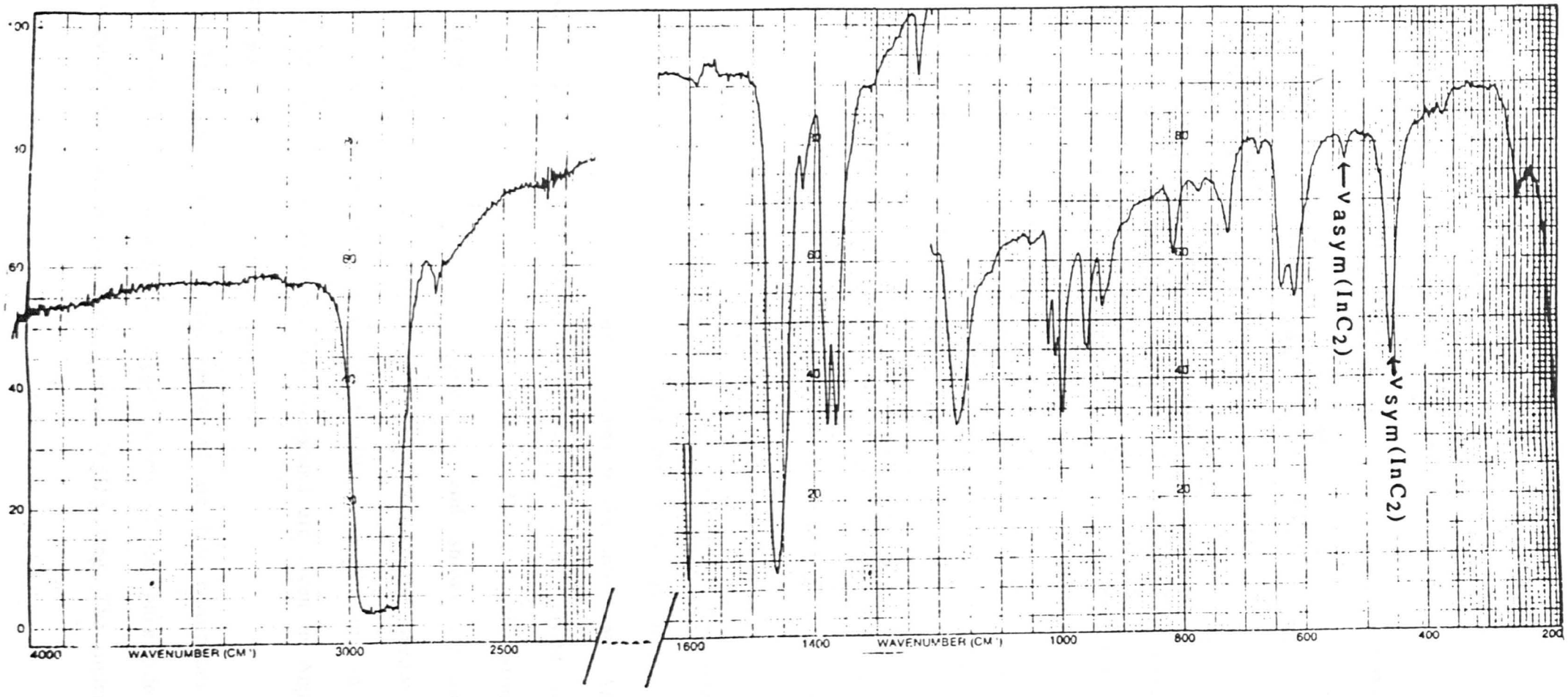
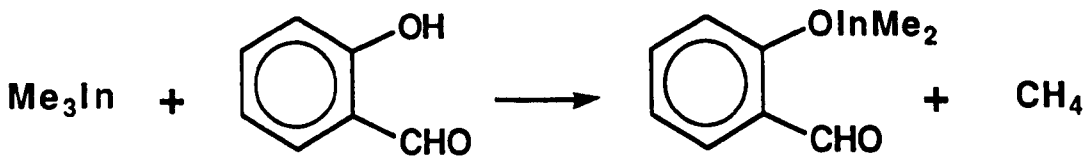


Diagram 5. Infra-red spectrum of $(Et_2InPBu^t_2)_2$ (Nujol mull between CsI plates).

Reaction of Trimethylindium with Salicylaldehyde.



This reaction was found to occur readily on the addition of one equivalent of salicylaldehyde to a hexane solution of trimethylindium at room temperature. The yellow powder thus formed was recrystallised from a dichloromethane/hexane mixture to give a yellow, crystalline solid. This solid was identified by microanalysis (C,H,In) and its ^1H-n.m.r. spectrum. This showed a singlet at δ-0.02 ppm corresponding to the methyl groups as well as signals corresponding to the salicylaldehyde. The integrals of the signals were in the correct ratio for a dimethylindium derivative of salicylaldehyde (shown in equation above).

Since the reacting species contains a further functional group (CHO) it was of interest to see whether any interaction occurs between this group and the surrounding indium atoms in the solid state. An *X*-ray crystallographic study of this compound was therefore carried out. This showed that the product was in fact dimeric. The molecular structure of this compound is shown in Diagram 6, and shows the additional interesting feature that both the oxygen atoms of the phenoxide and aldehyde groups are involved in the bonding with the indium centres. The bond lengths and angles for this compound are given in Appendix B (page 196).

The indium atoms in this compound are five co-ordinate and the dimerisation occurs through the oxygen atoms of the phenoxide groups. This gives rise to an essentially planar In_2O_2 ring. The dimeric unit

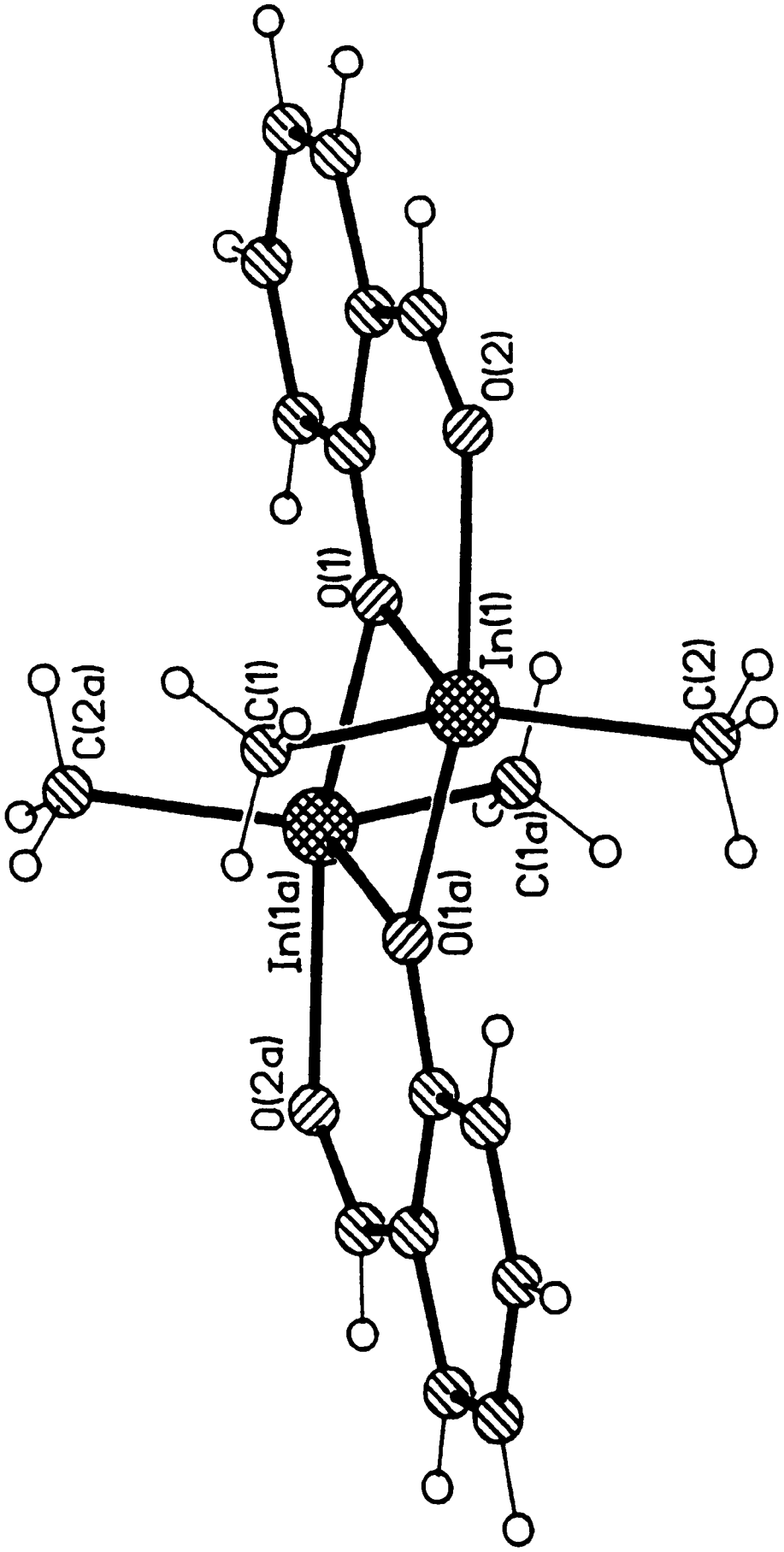


Diagram 6. View of the molecular structure of the dimeric salicylaldehyde derivative of trimethylindium as determined by a single-crystal *X*-ray crystallographic study. [Selected bond lengths (Å); In(1)-O(1), 2.188(3), In(1)-O(2), 2.341(4), In(1)-O(1a), 2.383(3), In(1)-C(1), 2.121(5), In(1)-C(2), 2.123(6). Selected bond angles (°); O(1)-In(1)-O(2), 79.9(1), O(1)-In(1)-O(1a), 74.8(1), In(1)-O(1)-In(1a), 105.2(1), C(1)-In(1)-C(2), 141.9(2).]

consists of five fused rings that are all approximately in the same plane. The In-O bonds in the In_2O_2 ring have different bond strengths. The strongest has a length of 2.188(3) Å and the weaker one has a length of 2.383(3) Å. The other In-O interaction with the oxygen atom of the aldehyde group has a length of 2.341(4) Å. Too few values for In-O bond lengths are known for any trends in these values to be properly rationalised. However, the values found here fall within the range found in previous studies of 2.15-2.45 Å.[102,113,140] The In-C bond lengths have a mean value of 2.122 Å. This falls within the expected range for In-C bonds of 2.05-2.25 Å that have previously been determined.[56,65,71,77,139]

This compound has the same basic structure and geometry around the metal as the gallium analogue.[49] Both have similar internal angles in the M_2O_2 rings. The M-O-M angles are 104.5(1)° (Ga) and 105.2(1)° (In) and the O-M-O angles are 75.5(1)° (Ga) and 74.8(1)° (In). The main difference is that in the gallium compound the metal-oxygen bonds that give rise to the dimerisation are much weaker than those in the indium compound. In the indium compound this bond has a length of 2.383(3) Å whereas in the gallium compound the corresponding bond has a length of 2.462(4) Å. The fact that the gallium-oxygen bond is longer is even more surprising when it is remembered that the gallium atom is smaller than an indium atom. Comparison of the indium-carbon and gallium-carbon bond lengths suggests that it is smaller by approximately 0.18 Å. Taking this difference in size into account makes the gallium-oxygen bond effectively 0.26 Å longer than that in the indium compound. The main reason for this is probably the steric crowding that would exist around the smaller gallium atom if the bond lengths forming the dimer

were shorter. For the larger indium atom this steric problem does not arise and so a much stronger dimeric association can occur.

This increase in bond strengths in the indium dimer can be readily seen in the mass spectra of the two compounds. The gallium analogue shows only peaks attributable to the monomer in its mass spectrum [141] whereas the indium compound with the stronger oxygen bridges exhibits peaks that are derived from both the monomer and the dimer. The mass spectrum of the indium compound is summarised in Table 4. The peak corresponding to the dimeric molecular ion could not be seen, however, a peak arising from the loss of only one methyl group from this dimer (m/z=517) was observed.

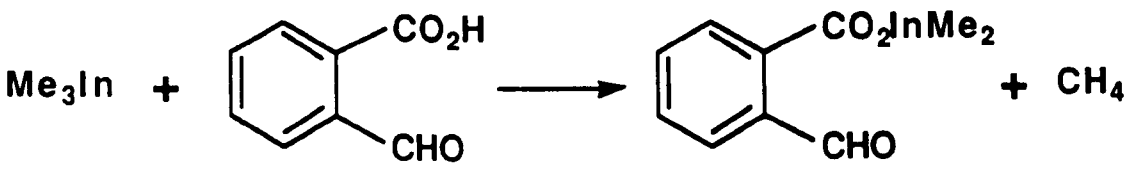
Table 4. Summary of the E.I. Mass Spectrum of the Salicylaldehyde Derivative.

m / z	Assignment	m / z	Assignment
517	$(D\text{-}Me)^+$	251	$(M\text{-}Me)^+$
428	$(D\text{-}C_6H_3CHO)^+$	236	$(M\text{-}2Me)^+$
411	$(D\text{-}C_6H_4CHO)^+$	145	$(Me_2In)^+$
266	M^+		

The infra-red spectrum of the compound showed several bands in the region 400-550 cm^{-1}. Assignments of the bands arising from the InC_2 stretching modes are accordingly tentative. The $\nu_{sym}(InC_2)$ band

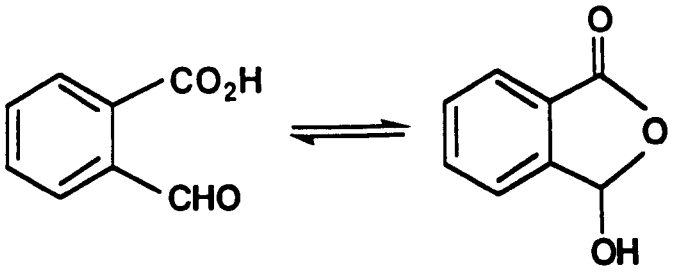
can be seen at 486 cm^{-1} and $\nu_{asym}(InC_2)$ is found at 533 cm^{-1}. These are in the expected ranges for these bands. The difference in frequency between these two bands is 47 cm^{-1} which predicts a C-In-C bond angle of approximately 144°. The value actually found in the crystal structure is 141.9° and so in this case the agreement between the predicted and experimental values for this bond angle is good.

Reaction of Trimethylindium with 2-Carboxybenzaldehyde.

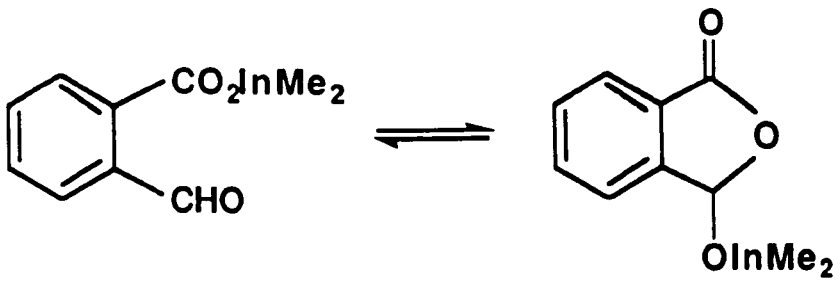


This reaction proceeds readily at room temperature on mixing a 1:1 mixture of trimethylindium and 2-carboxybenzaldehyde in hexane. The result was a clear colourless solution which on cooling precipitated a colourless powder. This was recrystallised from a THF/hexane mixture to give a microcrystalline product. The identity of this was confirmed by microanalysis (C,H,In) and by its ^{1}H-n.m.r. spectrum (DMSO solution). This showed a singlet at δ,-0.23 ppm corresponding to the methyl groups as well as signals characteristic of the 2-carboxybenzaldehyde. These signals had the correct integral ratios for the expected dimethylindium derivative.

Of particular interest in this reaction is the equilibrium that exists in solution for the starting material, 2-carboxybenzaldehyde [142]:-



This equilibrium provides two different types of acidic species in solution which are both capable of reacting with the trimethylindium. This gives rise to the possibility of one of two different products being formed or possibly an equilibrium mixture of the two :-



In the case of pure 2-carboxybenzaldehyde the equilibrium in the solid state has been shown by infra-red spectroscopy to lie entirely in the cyclised form.[142] However, in solutions (particularly dilute acids) the position of the equilibrium is shifted towards the ring opened species. In the ^{1}H-n.m.r. spectrum the two species can be differentiated by the resonance for the aldehyde proton. In the cyclised form this signal occurs at 6.75 ppm whereas in the ring-opened form this signal is observed at 10.15 ppm. Clearly then, in dimethylsulphoxide solution the dimethylindium derivative of this compound exists only in the ring opened form as the corresponding resonance occurs at 10.39 ppm. This, however, gives information only about the species present in this particular solvent and tells us nothing concerning the species present in the solid state. Indeed, dimethylsulphoxide has already been shown to

promote the ring opening of 2-carboxybenzaldehyde.[142] The compound was insoluble in most common solvents and so its ^{1}H-n.m.r. could not be obtained in a different solvent to DMSO .

The infra-red spectrum of the dimethylindium derivative shows bands at 1541 cm^{-1} and 1458 cm^{-1} which may be assigned as ν_{asym} and ν_{sym} respectively of a co-ordinated $-CO_2$ group. These bands compare well with those found for dimethylindium acetate [102] at 1535 cm^{-1} and 1455 cm^{-1} . There is also a band at 701 cm^{-1} which may correspond to the symmetrical deformation of the $-CO_2$ group that is found at 681 cm^{-1} in the spectrum of dimethylindium acetate. The carbonyl stretching band observed at 1667 cm^{-1} is close to that expected for a free aldehyde attached to an aromatic ring. Two bands can also be seen at 2730 cm^{-1} and 2680 cm^{-1} which correspond to those expected for the C-H stretching of an aldehyde group. In view of the peaks observed for a co-ordinated carboxylate group and a free aldehyde group it seems likely that the solid state structure of this compound is based upon the ring opened form.

The correlation between the infra-red spectrum of this compound and that of dimethylindium acetate also suggests that both of the oxygen atoms of the carboxylate group are co-ordinated to the indium atom as has been shown by *X*-ray crystallography for the acetate.[102] The bands corresponding to ν_{sym} and ν_{asym} of the InC_2 unit can be seen at 491 cm^{-1} and 536 cm^{-1}. The difference between these of 45 cm^{-1} would predict an InC_2 bond angle of approximately 142°. This is very close to that found for the similar dimethylindium salicylaldehyde compound and so this compound may also be further associated so giving the indium a co-ordination number greater than four. The infra-red spectrum suggests that it is unlikely that this association occurs through the aldehyde

oxygen atom and so the only other alternative is that one or both of the carboxylate oxygen atoms are bridging between two indium atoms.

The mass spectrum of this compound shows peaks derived from the monomer and a few very low intensity peaks derived from a dimer (only 0.4% of the total ion count). This suggests that any association in the solid state is only weak. The mass spectrum is summarised in Table 5.

Table 5. Summary of the E.I. Mass Spectrum of the 2-Carboxybenzaldehyde Derivative.

m / z	Assignment	m / z	Assignment
443	$(D\text{-}Me_2In)^+$	279	$(M\text{-}Me)^+$
323	$(M+CHO)^+$	251	$(M\text{-}Me\text{-}CO)^+$
308	$(M+CHO\text{-}Me)^+$	235	$(M\text{-}2Me\text{-}CHO)^+$
294	M^+	145	$(Me_2In)^+$

In view of the evidence of the ^1H-n.m.r., infra-red and mass spectra the likeliest solid state structure is a dimethylindium unit bonded to both of the carboxylate oxygen atoms. The aldehyde oxygen atom does not appear to be co-ordinated but it seems likely that a weak association occurs through the carboxylate group. Such association is found in the structure of dimethylindium acetate [102] which has both oxygen atoms of the acetate group co-ordinated to a single indium atom. These oxygen atoms are then further weakly co-ordinated to indium

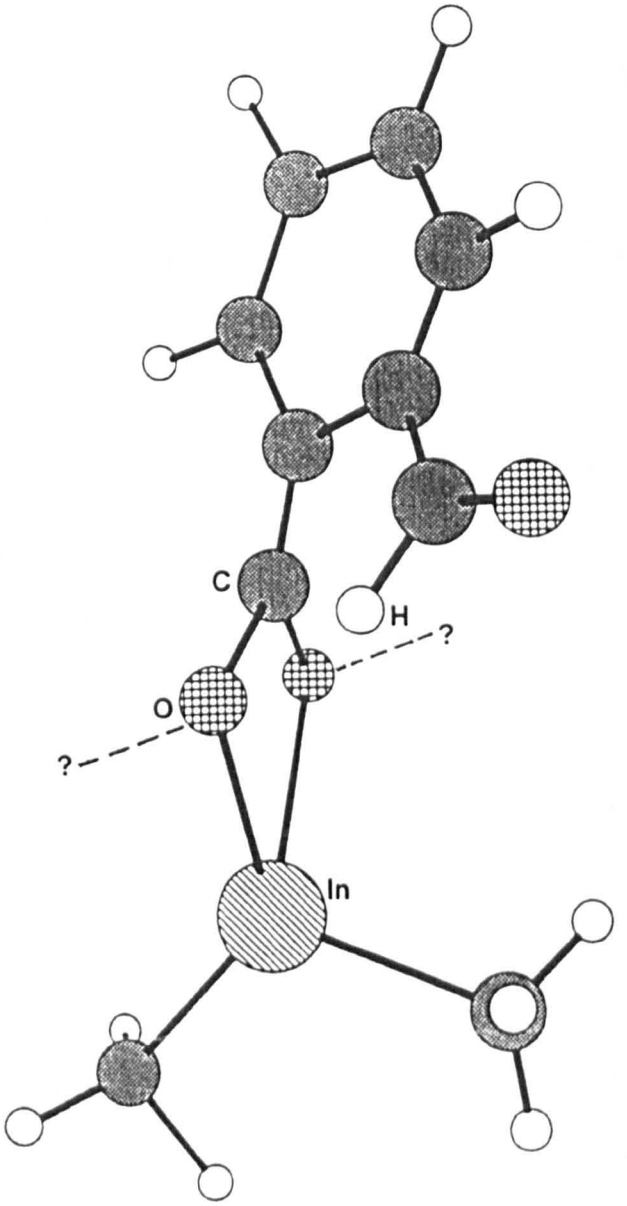
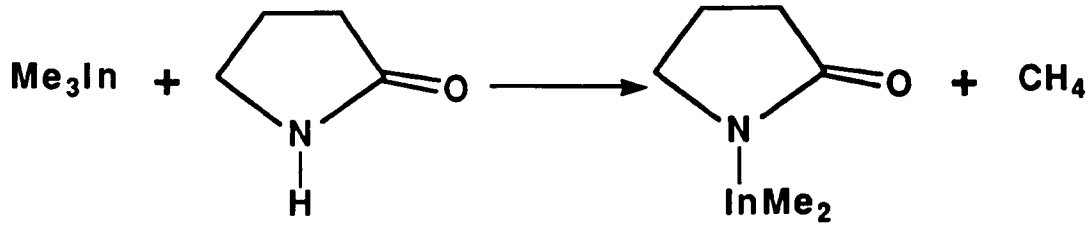


Diagram 7. View of a model of the proposed structure of the 2-carboxybenzaldehyde derivative of trimethylindium.

atoms in neighbouring molecules. The structure that is envisaged is shown in Diagram 7.

Reaction of 2-Pyrrolidinone with Trimethylindium.



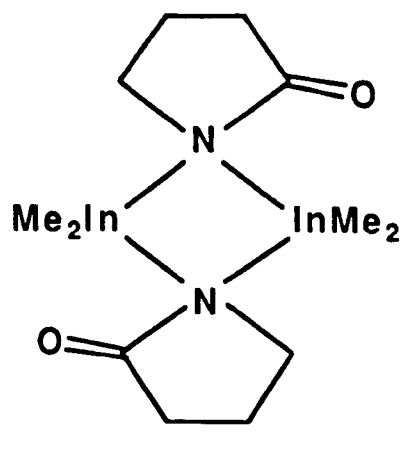
This reaction was found to occur readily at room temperature on mixing a 1:1 mixture of 2-pyrrolidinone and trimethylindium in toluene. This resulted in a colourless solution which after mixing with hexane and cooling, precipitated a colourless microcrystalline solid. The identity of this product was confirmed by microanalysis (C,H,N,In) and its ^{1}H-n.m.r. spectrum. This showed a singlet at δ-0.62 ppm corresponding to the methyl groups and two multiplets corresponding to the 2-pyrrolidinone. These signals had the correct integral ratios for the predicted dimethylindium derivative of the 2-pyrrolidinone (see equation above).

The mass spectrum of the product showed peaks that could be assigned as deriving from both the monomer and the dimer. There were also some very low intensity peaks at masses higher than that of the dimer which could not be assigned. These increased in intensity as the source temperature increased and so it is likely that they were due to reactions occurring in the chamber. The mass spectrum is summarised in Table 6.

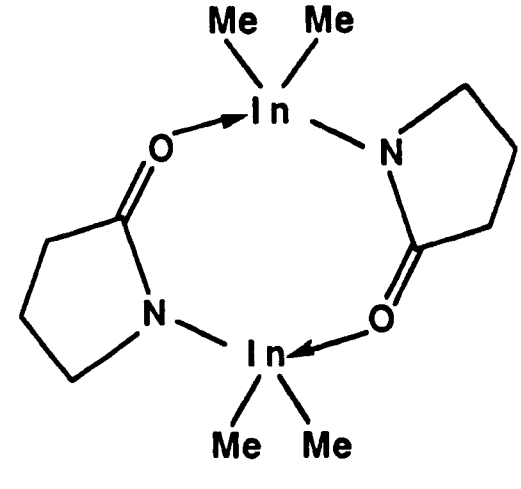
Table 6. Summary of the E.I. Mass Spectrum of 2-Pyrrolidinone Derivative.

m / z	Assignment	m / z	Assignment
443	$(D\text{-}Me)^+$	214	$(M\text{-}Me)^+$
427	$(D\text{-}2Me)^+$	199	$(M\text{-}2Me)^+$
413	$(D\text{-}2Me\text{-}CH_2)^+$	145	$(Me_2In)^+$

If there is a correlation between the mass spectrum and the solid state structure then the dimer peaks in the mass spectrum suggest that the compound is likely to be dimeric. This suggests two possible structures. These are shown in Diagram 8.



Type (I)



Type (II)

Diagram 8. The two possible structures for the 2-pyrrolidinone derivative of trimethylindium.

Comparisons of the infra-red spectra of 2-pyrrolidinone and the product might reasonably be expected to differentiate between these two possible structures in the solid state. Type (I) with only the nitrogen atoms involved in the bonding would be expected to show very little change in the frequency of the carbonyl stretching band. Type (II) on the other hand involves bonding with both the nitrogen atoms and the oxygen atoms of the carbonyl groups and would, therefore, be expected to show significant changes in the carbonyl stretching bands. The infra-red spectrum of 2-pyrrolidinone shows a band at 1685 cm^{-1} corresponding to the carbonyl stretch. On reaction with trimethyl indium this band shifts to 1581 cm^{-1}. This represents a significant change in the bonding of the carbonyl group and shows that this group is actively involved in the bonding in the dimethylindium derivative. This indicates that structure type (II) is the preferred conformation rather than a structure of type (I).

Diagram 9 shows a model of the structure that is envisaged. The structure consists of a puckered eight membered ring containing two indium atoms forming the dimer. Such a structure has previously been found for the dimethylacetamidine derivative of trimethylindium.[143] This comparison is predictable when the similarities of the two functional groups of these systems are compared. For dimethylacetamidine these are N-C=N whereas for 2-pyrrolidinone these are N-C=O.

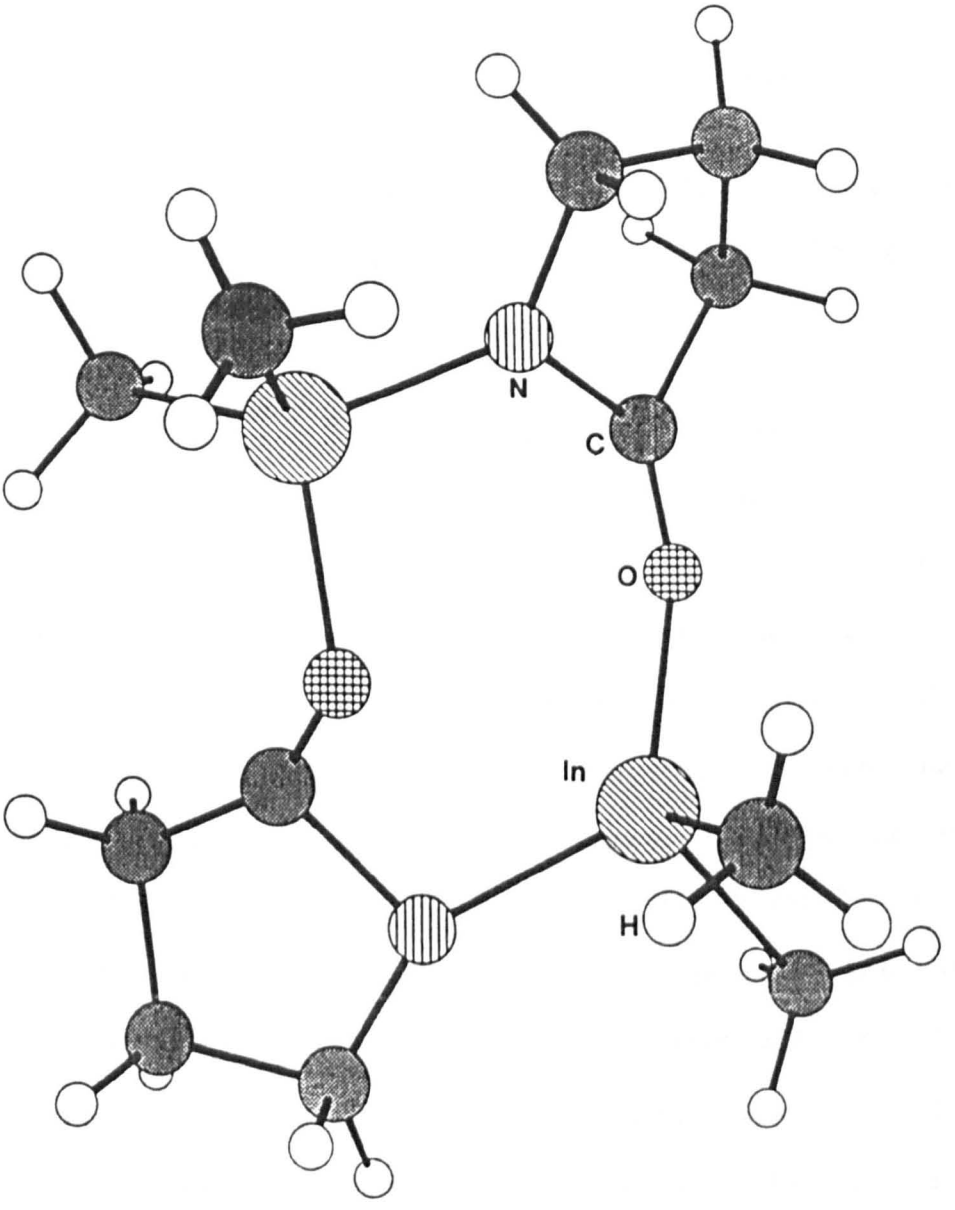
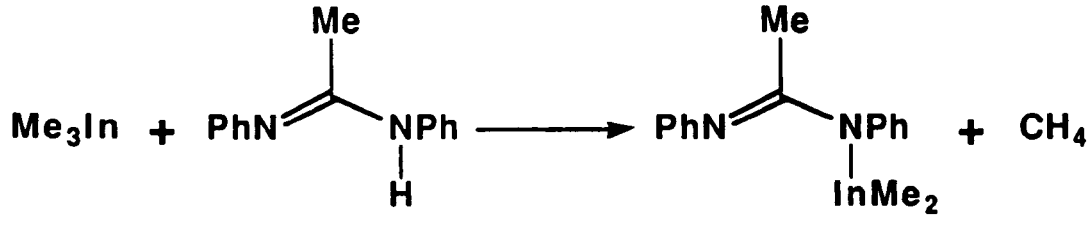


Diagram 9. View of a model of the proposed structure of the 2-pyrrolidinone derivative of trimethylindium.

Reaction of Diphenylacetamidine with Trimethylindium.



This reaction was found to occur readily at room temperature on mixing trimethylindium with diphenylacetamidine in a 1:1 ratio in toluene. The result was a pale yellow solution which after concentrating, mixing with hexane and cooling gave a colourless precipitate. This was recrystallised from hexane to give a colourless crystalline solid. The identity of this product was confirmed by microanalysis (C,H,N) and its ^{1}H-n.m.r. spectrum. The spectrum showed a singlet at δ 0.03 ppm corresponding to the methyl groups bonded to the indium. The signal corresponding to the methyl group of the diphenylacetamidine could be seen at δ 1.58 ppm and the remaining signals were in the aromatic region of the spectrum (6.90 and 7.13 ppm). These signals all had the correct integral ratios for the predicted product (see above equation).

Table 7. Summary of the E.I. Mass Spectrum of the Diphenyl-acetamidine Derivative.

m/z	Assignment	m/z	Assignment
694	$(D\text{-}Me+H)^+$	339	$(M\text{-}Me)^+$
548	$(D\text{-}3Me\text{-}In)^+$	324	$(M\text{-}2Me)^+$
533	$(D\text{-}4Me\text{-}In)^+$	310	$(M\text{-}3Me+H)^+$
354	M^+	145	$(Me_2In)^+$

The mass spectrum of this compound is summarised in Table 6. This showed peaks that could be assigned as fragments of both a monomer and a dimer and it is therefore likely that this compound is dimeric in the solid state. This dimeric formulation is in agreement with the known structures of some related compounds that have been reported. An *X*-ray crystallographic study of dimethylgallium-N,N′-dimethylacetamidine has previously been reported. This compound was found to be dimeric with an eight membered puckered ring.[143] It seems likely, therefore that this dimeric dimethylindium derivative has a similar structure.

The infra-red spectrum of this compound also shows several similarities to the spectrum of the previously reported dimethylindium-N,N′-dimethylacetamidine. For this dimethyl-acetamidine compound, bands at 1468 cm^{-1} and 1540 cm^{-1} were assigned as ν_{sym} and ν_{asym} stretching modes for the CN_2 unit. For the diphenylacetamidine these

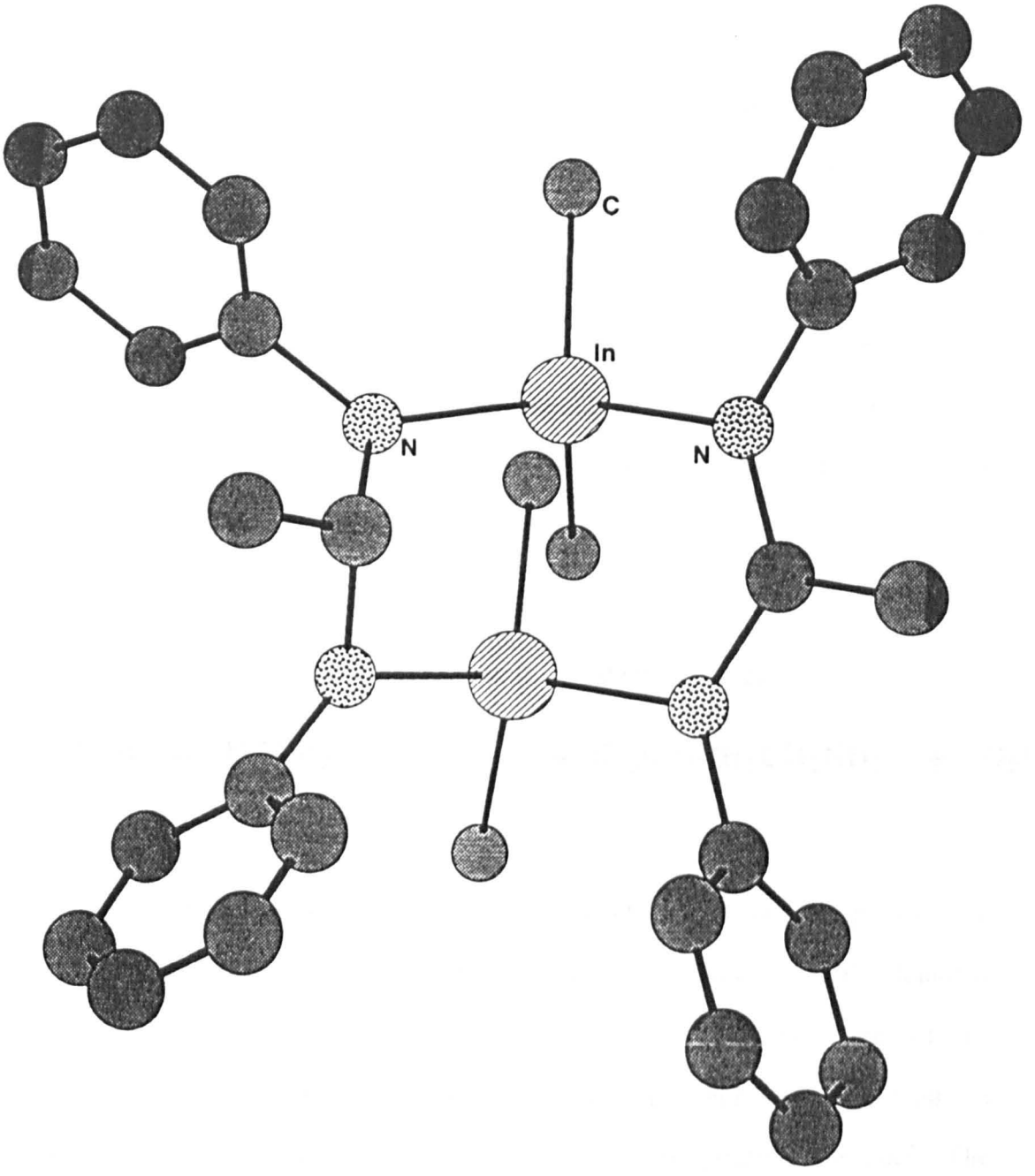


Diagram 10. View of a model of the proposed structure of the diphenyl-acetamidine derivative of trimethylindium.

bands were observed at 1475 cm^{-1} and 1528 cm^{-1} respectively. Similarly a band observed at 384 cm^{-1} in the dimethylacetamidine compound was assigned as a symmetrical stretching mode of the InN_2 unit. This band was observed at 392 cm^{-1} in the present diphenylacetamidine compound.

The similarities in the infra-red spectra of these compounds is further evidence that this diphenylacetamidine compound has a dimeric structure with an eight membered ring. A model of the structure that is envisaged is shown in Diagram 10.

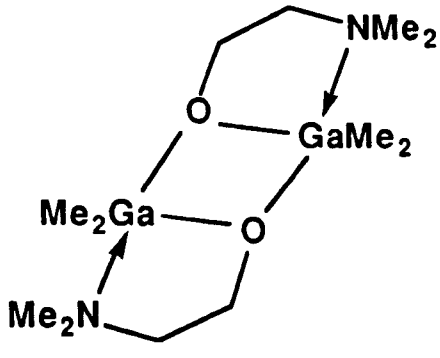
Reaction of Triethylindium with Ethanolamine.

$$Et_3In + HOCH_2CH_2NH_2 \longrightarrow Et_2InOCH_2CH_2NH_2 + C_2H_6$$

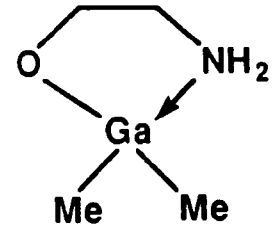
This reaction was found to occur readily at room temperature on mixing ethanolamine with triethylindium in a 1:1 ratio in THF. Removal of the solvent under reduced pressure, after a reaction time of 10 minutes, left a colourless powder. This was recrystallised from a THF/hexane mixture to give a colourless, microcrystalline product. The identity of the product was confirmed by microanalysis (C,H,N,In) and its ^{1}H-n.m.r. spectrum. The spectrum showed the expected triplet (δ1.50 ppm) and quartet (δ0.65 ppm) for the ethyl groups bonded to the indium as well as signals characteristic of the ethanolamine, a broad triplet (δ0.31ppm, NH_2), a multiplet (δ2.22 ppm, CH_2) and a triplet (δ0.65 ppm, CH_2). The integrals of these signals were in the correct ratios for the predicted product (see above equation). The broad triplet which was assigned to the amino-group confirms that the ethane elimination

occurred with the alcohol group. This is expected on the grounds that the alcohol group is more acidic than the amino group.

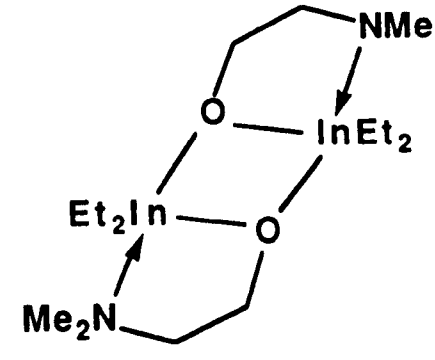
Some related compounds to this have previously been reported. The dimethylgallium derivatives of ethanolamine and dimethylethanolamine as well as the diethylindium derivative of dimethylethanolamine have all been prepared and their structures deduced. The structures of these are shown below.[116,144,145]



(I)



(II)



(III)

The mass spectrum of the diethyl(ethanolamino)indium compound showed peaks arising from a monomer (m/z=234) and a dimer (m/z=467) as well as peaks at even higher mass values that could not be assigned. The mass spectrum is summarised in Table 8.

Table 8. Summary of the E.I. Mass Spectrum of the Ethanolamine Derivative.

m / z	Assignment	m / z	Assignment
565	-	406	$(D-2Et+2H)^+$
551	-	234	$(M+H)^+$
467	$(D+H)^+$	204	$(M-Et)^+$
437	$(D-Et)^+$	173	$(Et_2In)^+$

The mass spectrum of compound (II) (above) also shows peaks attributable as a monomer, a dimer and higher oligomers.[145] This compound was shown by *X*-ray crystallography to have a monomeric structure in which the monomers were linked by hydrogen bonding. In the diethylindium analogue prepared here there is similar scope for hydrogen bonding and so a similar mass spectrum would be expected if this were the case.

Very little infra-red data has been reported for any of these compounds and so comparisons with the infra-red spectrum of the compound prepared here are not possible. The bands in the infra-red spectrum at 461 and 493 cm^{-1} and can be assigned as the $\nu_{sym}(InC_2)$ and the $\nu_{asym}(InC_2)$ modes respectively. The difference between these two modes suggests an C-In-C bond angle of approximately 124°. This value would be reasonable for either of the two possible structures. In the

absence of any other evidence it is impossible to differentiate between the different structures that are possible.

Reaction of Triethylindium with Phenylethyne.

$$Et_3In + HC{\equiv}CPh \longrightarrow Et_2InC{\equiv}CPh + C_2H_6$$

This reaction occurred on warming the reactants in a 1:1 ratio at 60 °C in hexane. Removal of the solvent under reduced pressure left a cream coloured product which was impure (according to its ^{1}H-n.m.r. spectrum). Attempting to recrystallise this product, it was found that it would only precipitate from solution on the addition of one equivalent of triphenylphosphine and so it could only be isolated as its triphenylphosphine adduct. The identity of this adduct was confirmed by microanalysis (C,H,In) and its ^{1}H-n.m.r. spectrum. The spectrum showed the expected triplet (δ1.64 ppm) and quartet (δ1.08 ppm) for the ethyl groups bonded to the indium as well as signals in the aromatic region (7.0 and 7.3) corresponding to the triphenylphosphine and the phenyl group in the phenylethyne. These signals had the correct integral ratios for the expected product (see above equation).

The dimethylindium analogue of this compound, $Me_2InC{\equiv}CPh$, has previously been reported.[121] This compound is believed to be dimeric in the solid state with bridging phenylethynyl groups. The infra-red spectrum of this analogue in benzene solution shows a band at 2050 cm^{-1} corresponding to the C≡C stretch. In THF solution this band was shifted to 2110 cm^{-1} which was interpreted as showing that in benzene the phenylethynyl groups are bridging and that in THF the donor solvent molecules break these bridges. In the adduct prepared here the

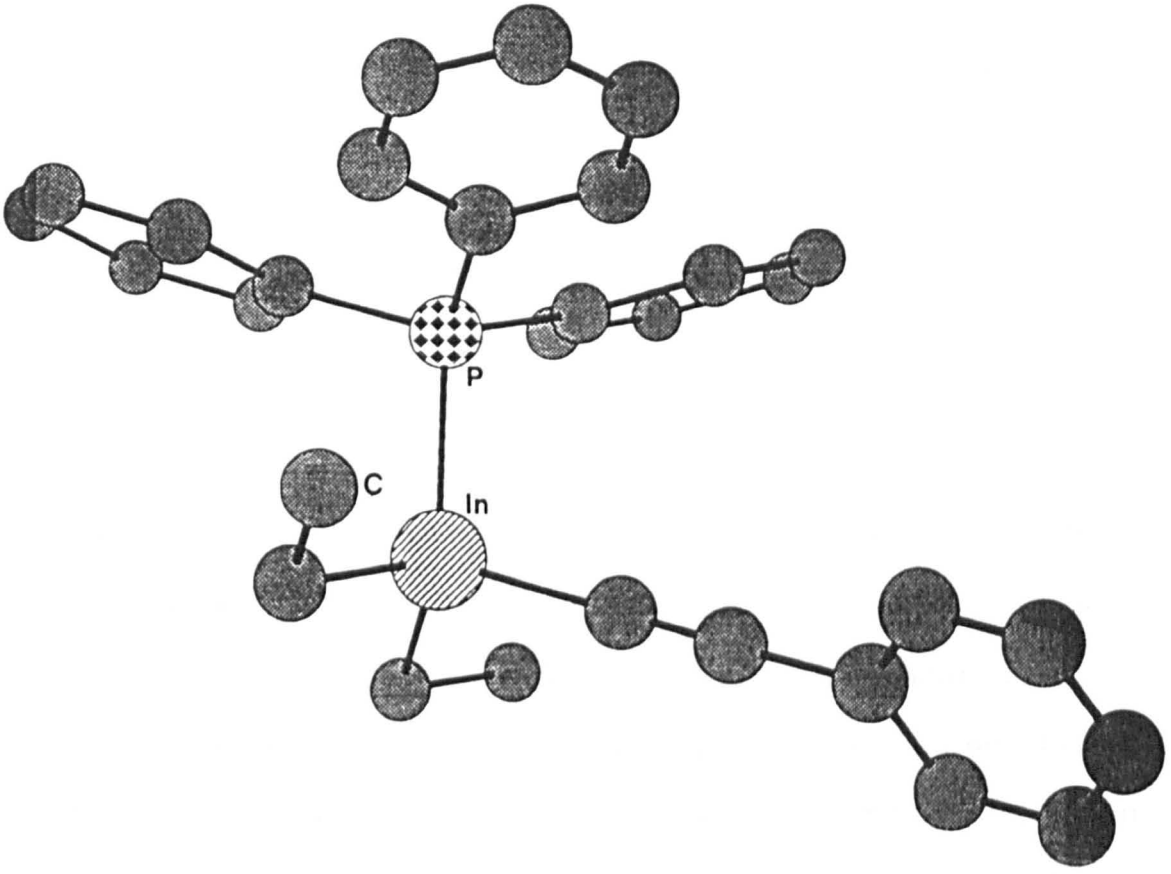


Diagram 11 . View of a model of the proposed structure of the triphenylphosphine adduct of diethyl(phenylethynyl)indium.

corresponding band is observed at 2080 cm^{-1} which is midway between the values found in solution for the bridging and non-bridging cases. It is unlikely that the phenylethynyl groups are acting as bridging ligands in this adduct and so the difference in frequency between this band and the band found for $Me_2InC{\equiv}CPh$ in THF solution is probably due to an effect of the triphenylphosphine ligand bonded to the indium atom.

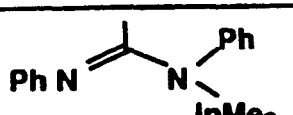
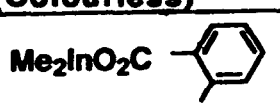
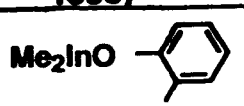
The infra-red spectrum in the region 400-550 cm^{-1} is complicated and shows several bands. Accordingly it is not possible to assign specific In-C stretches with any degree of certainty. However, by comparison with the spectrum of the diethyl(ethanolamino)indium compound the bands at 465 and 507 cm^{-1} can be tentatively assigned as the $\nu_{sym}(InC_2)$ and the $\nu_{asym}(InC_2)$ modes respectively. The difference between these two bands (42 cm^{-1}) suggests a C-In-C bond angle of approximately 138°. This is a little on the large size for a four co-ordinate monomer, however, there is no evidence to suggest an alternative structure to this monomer. In the absence of any other evidence, it must be concluded that a four co-ordinate monomer is the likeliest structure for this complex. A model of the envisaged structure is shown in Diagram 11.

Conclusions.

The compounds that have been prepared, some of their physical properties and their infra-red spectra are summarised in Table 9.

A clear structural trend for these organoindium derivatives is that where it is sterically possible the indium atoms increase their co-ordination number through oligomerisation. This can be particularly seen for the salicylaldehyde derivative which could exist as a four co-

Table 9

Compound	Association	M.Pt. (°C)	Infra-Red Spectrum (cm^{-1}) (a)
$Et_2InPBu^t_2$ (Colourless)	Dimer	265 (dec)	463(s),529(vw),620(m),641(m),821(m),936(m),961(m), 1003(s),1025(m),1173(s),1234(w),1390(w).
$Et_2InOCH_2CH_2NH_2$ (Colourless)	–	–	322(w),383(m),461(m),493(m),576(m),609(m),901(s), 948(m),1007(w),1053(m),1082(s),1107(m),1580(w).
$Et_2InC{\equiv}CPh.PPh_3$ (Colourless)	Monomer	–	432(w),465(w),507(S),519(m),546(m),651(m),700(s),749(m), 762(s),936(m),965(m),1003(m),1021(m),1084(m),1102(s),1165(m), 1209(w),1237(w),1443(s),1577(m),1594(m),1602(m),2080(w).
 (Colourless)	Dimer	130-132	245(m),490(m),520(s),699(s),892(w),913(w),930(w), 1009(w),1111(s),1155(m),1304(s),1581(s).
 (Colourless)	Dimer	82-85	296(m),392(m),433(m),457(m),486(m),518(s),569(m),696(s), 749(m),831(m),899(m),1003(m),1017(m),1073(m),1170(m),1221(m), 1268(m),1307(m),1369(s),1423(br),1495(br),1572(s),1596(m).
 (Colour-less)	–	212-216	437(m),491(m),536(s),644(m),699(s),740(s),824(m), 907(m),1080(br),1155(m),1194(s),1403(s),1458(s), 1541(s),1577(s),1601(w),1648(s),1667(s),
 (Yellow)	Dimer	188-192	244(m),310(br),486(m),520(s),533(m),591(m),765(m), 896(s),1048(m),1129(w),1156(m),1180(m),1291(s), 1415(m),1447(sh),1545(m),1602(s),1642(sh).

(a) Nujol mull between CsI plates.

ordinate monomer, but actually dimerises to give a species with five co-ordinate indium atoms.

A point to be considered is the mechanism by which these reactions proceed. In most cases, the likeliest pathway involves co-ordination of the acidic species followed by a rearrangement to eliminate the alkane. Indeed, previous work has shown that for some secondary phosphines and amines the corresponding trialkylindium adduct is stable at room temperature and only eliminates alkane on heating.[137] For the reactions carried out here, this mechanism appears to be the most likely. However, it is worth considering the case of the reaction carried out with phenylethyne. For this mechanism to hold, an adduct would have to be formed between this alkyne and triethylindium to allow the elimination reaction to proceed. No adducts of this type have ever been reported for either gallium or indium trialkyls and it is unclear whether or not a strong interaction between the two species could occur in solution. The crystal structure of $Me_2InC{\equiv}CMe$ has shown that such alkyne-indium interactions can exist in the solid state. It has also been shown that this compound is dimeric in solution and the gas phase and this dimerisation is believed to occur via a bond between the p electrons of the alkyne and the vacant indium p_z orbital.[56] It is therefore possible that an alkyne-trialkylindium complex could exist in solution and that the alkane elimination could occur via this adduct.

A possible alternative to this mechanism involves the formation of free radicals in solution. The formation of an ethyl radical followed by hydrogen abstraction from the alkyne would lead to the same products. This is shown schematically in Diagram 12.

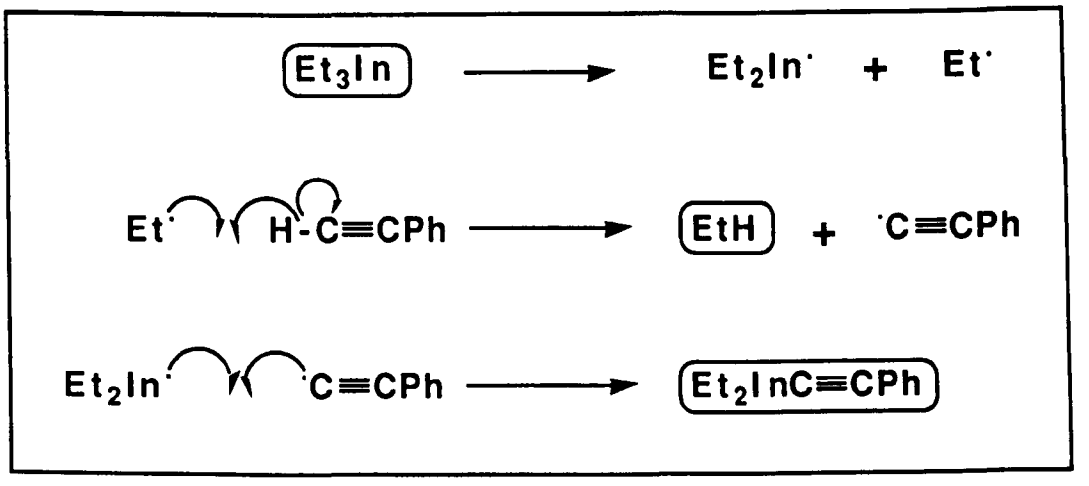


Diagram 12. Schematic representation of the possible free radical pathway for the reaction between triethylindium and phenylethyne.

In an attempt to investigate this possibility, the reaction of triethylindium with the stable free radical TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, free radical) was studied. Initially this reaction produced a very deep red solution in hexane at -78 °C. This turned into a colourless solution on warming over a period of a few minutes. From this solution was obtained a colourless, crystalline solid that was very unstable. For this reason a proper characterisation of this compound was not possible. However, microanalysis and the ^{1}H-n.m.r. spectrum of the solid suggested that it was the diethylindium derivative of TEMPO. Although it may be possible for this reagent to react via another mechanism, it is possible that this product was formed by a free radical mechanism with the loss of an ethyl radical. Although this is not conclusive, the fact that the reaction occurred so readily with this radical species in solution offers some support to the possibility of a free radical pathway for these reactions.

The mechanism that actually occurs probably depends upon the nature of the acidic species involved. For the more acidic species that

readily form strong donor-acceptor bonds with indium trialkyls such as alcohols, the most important mechanism is likely to be that which proceeds via the adduct. However, for less acidic species that do not readily form complexes with the indium trialkyls it is likely that a free radical process is more important.

CHAPTER 5

THERMAL DECOMPOSITION OF ORGANOINDIUM COMPOUNDS

Introduction.

An important application of organoindium compounds is their use as precursors in the preparation of semiconducting materials such as indium phosphide (InP) and gallium arsenide (GaAs), commonly known as the III-V semiconductors.

For this specialised use indium phosphide needs to be deposited in very thin layers, often only a few tens of atoms thick. The normal method by which this is achieved is by a process known as metallo-organic vapour phase epitaxy (MOVPE). This typically involves the thermal decomposition of a mixture of trimethylindium and phosphine gas (PH_3) onto a heated support at temperatures in the region of 600 °C, either at atmospheric or reduced pressure.[88,89] The reactants are usually supplied to the reaction chamber in a carrier gas of hydrogen. This thermal decomposition proceeds according to the following equation:-

$$In(CH_3)_3 + PH_3 \xrightarrow{600\ ^\circ C} InP + 3CH_4$$

The major drawback to this process are the two reagents. The extreme toxic properties of phosphine gas are well documented [146] and trimethylindium spontaneously ignites on contact with oxygen. For this reason it has been desirable to search for other safer precursors for the preparation of indium phosphide.

Recent work [1] has shown that compounds such as $(Me_2InPBu^t_2)_2$ and $(Me_2GaAsBu^t_2)_2$ can be thermally decomposed to give indium phosphide and gallium arsenide respectively. In the case of $(Me_2GaAsBu^t_2)_2$, the thermal decomposition has been shown to proceed

with elimination of methane and 2-methylpropene as the major hydrocarbon products. It was suggested that the mechanism involves the transfer of a hydrogen atom from a *t*-butyl group to a methyl group followed by elimination of the two gases. The structure of this compound determined by an *X*-ray crystallographic study showed that there was a close Ga-H interaction of 2.62 Å and it was suggested that this was involved in the decomposition reaction.[1] This scheme is shown in Diagram 1.

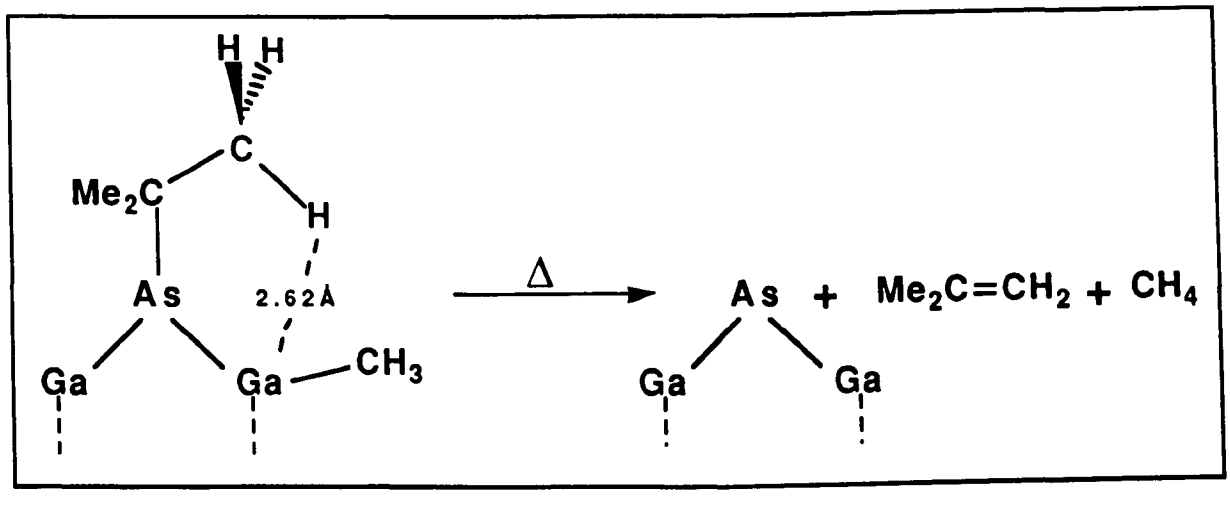


Diagram 1. Reaction scheme for the thermal decomposition of $(Me_2GaAsBu^t_2)_2$.[1]

Thermal Decomposition of $(Et_2InPBu^t_2)_2$.

In an effort to obtain more information concerning this type of reaction the thermal decomposition of $(Et_2InPBu^t_2)_2$ was studied in detail.

A small sample of $(Et_2InPBu^t_2)_2$ was heated slowly up to a temperature of 700 °C in a quartz vessel under nitrogen at atmospheric pressure. At regular intervals (every 100 °C rise in temperature) a

sample of the gas inside the apparatus was removed using a gas tight syringe and analysed using GC-mass spectroscopy. The gases, after being separated by a gas chromatography column, were identified by their characteristic mass spectra.[147] These spectra showed that below 200 °C very little gas evolution occurred. Above 200 °C four gases were observed, ethene, ethane, 2-methylpropene and 2-methylpropane. Above 500 °C a smaller quantity of propene was also observed. No other changes were observed during the heating. The final gas chromatogram, which was obtained after the sample had been heated to 700 °C, is shown in Diagram 2. This shows the peaks corresponding to ethane and ethene clearly, however, the 2-methylpropene and 2-methylpropane were not properly separated under the conditions used. The presence of these two gases was confirmed by comparing mass spectra taken at either side of the corresponding peak. The mass spectra obtained and the characteristic mass spectra of the gases that were identified are shown in Table 1.

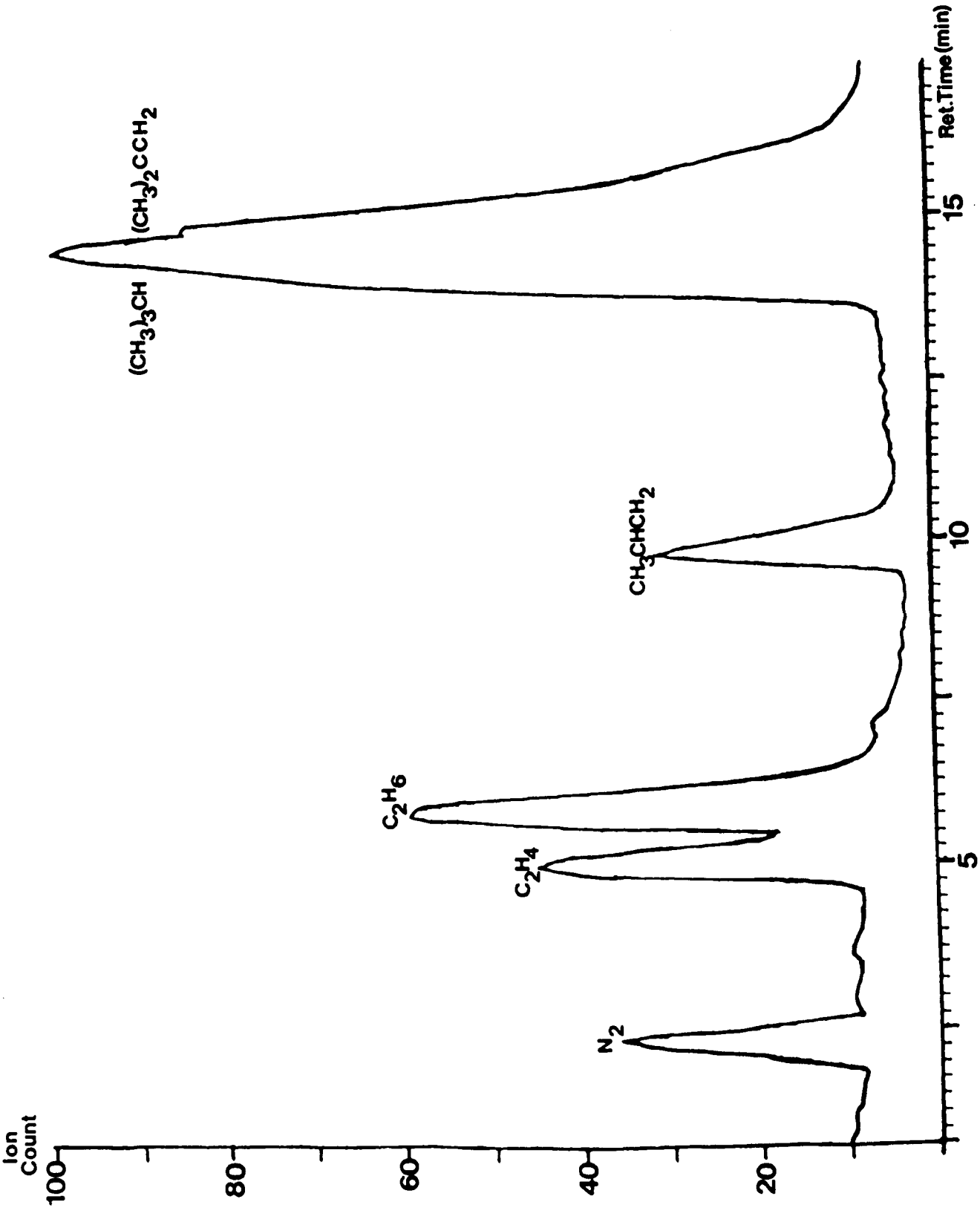


Diagram 2. GC trace of the gases produced during the thermal decomposition of $(Et_2InPBu^t_2)_2$. The gas sample was taken after heating to 700 °C.

Table 1. Main peaks observed in the E.I. mass spectra of the hydrocarbon gases separated during the thermal decomposition of $(Et_2InPBu^t_2)_2$. The literature mass spectra are summarised in parenthesis.[84]

Hydrocarbon	Mol.Wt	Observed Ions. (in order of abundance)
2-Methyl-propane	58	**43 42 41 27 39 28 57 44** (43 41 42 27 39 29 57 44)
2-Methyl-propene	56	**56 41 39 55 28 43 27 29** (41 56 39 55 28 27 40 29)
Propene	42	**41 39 42 40 27 38 28 26** (41 39 42 27 40 38 37 26)
Ethane	30	**28 30 27 29 26 25** (28 27 30 26 29 25)
Ethene	28	**28 27 26 25** (28 27 26 25)

The formation of all of the gases except propene can be easily rationalised in terms of hydrogen abstraction by either the *t*-butyl groups or the ethyl groups (see Diagram 3).

No information concerning the exact mechanisms involved in the formation of the observed gases was obtained. The structure of $(Et_2InPBu^t_2)_2$ that was determined (see Chapter 4, page 128) gives no insight into the mechanism. The hydrogen atoms were not located in this study, however, when they are inserted in idealised positions it can be seen that there are no close In-H interactions. The closest such interaction is 3.23 Å. This is significantly longer than the value found in $(Me_2GaAsBu^t_2)_2$ of 2.62 Å (even when the difference of approximately 0.18 Å in covalent radii between gallium and indium atoms is taken into account). So, contrary to the suggestions made by

Cowley *et al*,[1] a close metal-hydrogen interaction would not appear to be involved in the mechanism of the thermal decomposition.

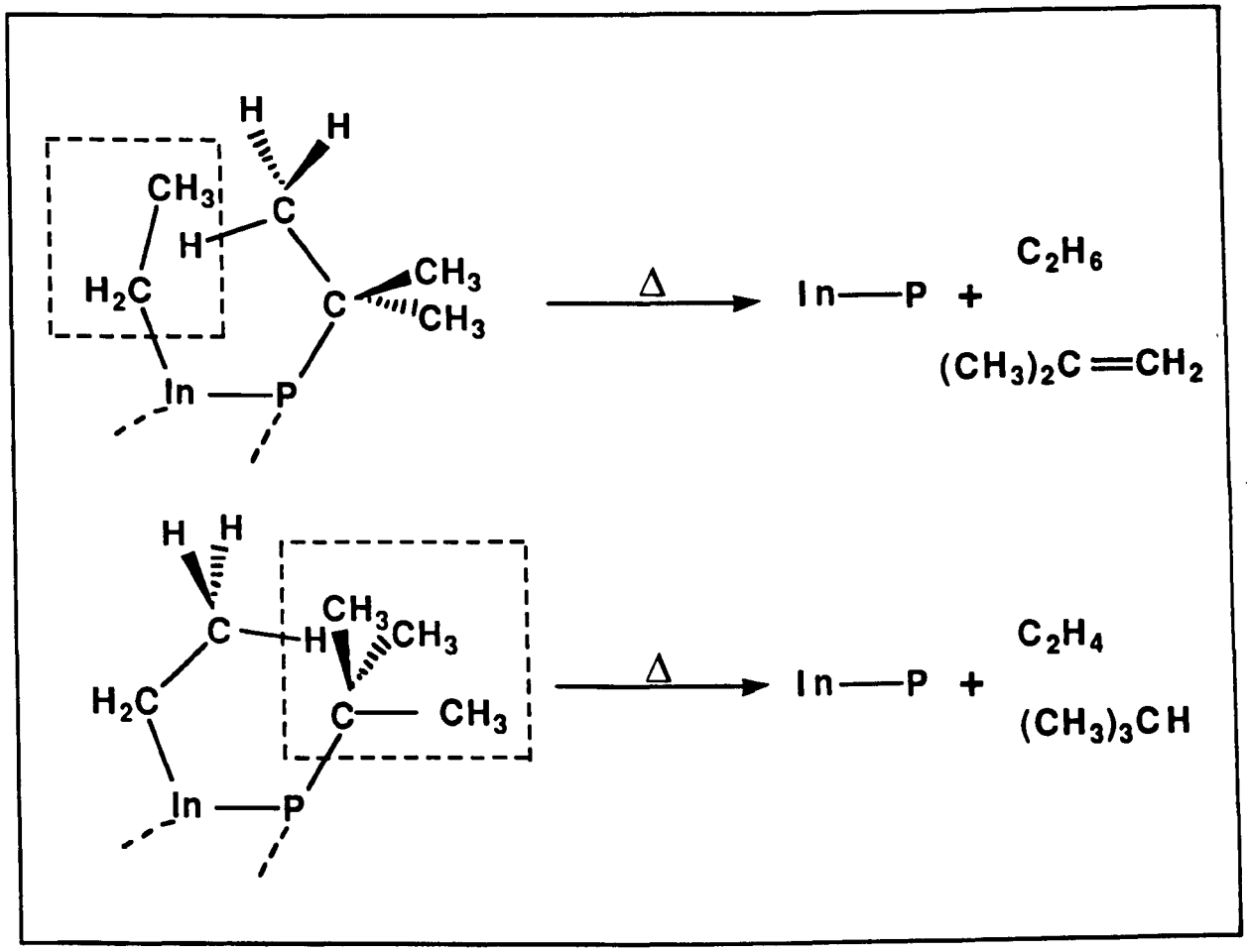


Diagram 3. Schematic representation of the two possible decomposition pathways that are possible for $(Et_2InPBu^t_2)_2$.

The small quantity of propene observed at higher temperatures could have been formed as a result of the thermal decomposition reaction, in which case a complicated reaction mechanism is indicated. Alternatively, it could have resulted from a high temperature reaction involving the hydrocarbons that had already been eliminated. This is the likeliest explanation in view of the known thermal properties of 2-methylpropene.[80] It has been shown that above 500 °C this hydrocarbon "cracks" in a complicated manner to give propene and

ethane. The temperature that this reaction is known to occur at is also within the range of temperatures that were used in this thermal decomposition reaction.

During the course of the reaction a colourless liquid was seen to condense in the cooler parts of the apparatus. This liquid fumed in air and had a characteristic phosphine type smell. The mass spectrum of this liquid showed peaks corresponding to $Bu^t_2PPBu^t_2$ and also to triethylindium. This was also confirmed by the ^1H-N.m.r. spectrum which showed a strong doublet corresponding to the *t*-butyl groups as well as a more complex set of weaker peaks in the range δ 1-2 ppm.

The fact that the main side products of this reaction are triethylindium and $Bu^t_2PPBu^t_2$ gives important information concerning the processes that occur during the decomposition. It is well known that heating organoindium compounds promotes exchange of the organo groups and so for $(Et_2InPBu^t_2)_2$ the following equilibrium would occur on heating:-

$$(Et_2InPBut_2)_2 \rightleftharpoons Et_3In + EtIn(PBu^t_2)_2$$

This explains the formation of triethylindium, however, less obvious is the pathway by which the biphosphine is formed. It was mentioned in Chapter 3 (page 118) that attempts to prepare species of the type $RIn(PBu^t_2)_2$ nearly always resulted in decomposition. It was also shown that $In(PBu^t_2)_3$ readily decomposed on heating to give the biphosphine. It is likely, therefore, that the biphosphine formed in the thermal decomposition of $(Et_2InPBu^t_2)_2$ is actually a result of the decomposition of $EtIn(PBu^t_2)_2$.

Any proposed mechanism by which this biphosphine is formed from these phosphido-indium compounds would have to explain why

indium compounds with one or three phosphido groups are stable at room temperature, whereas compounds with two such groups are unstable. A mechanism that can explain these observations involves intra-molecular formation of the biphosphine. This is shown schematically in Diagram 4.

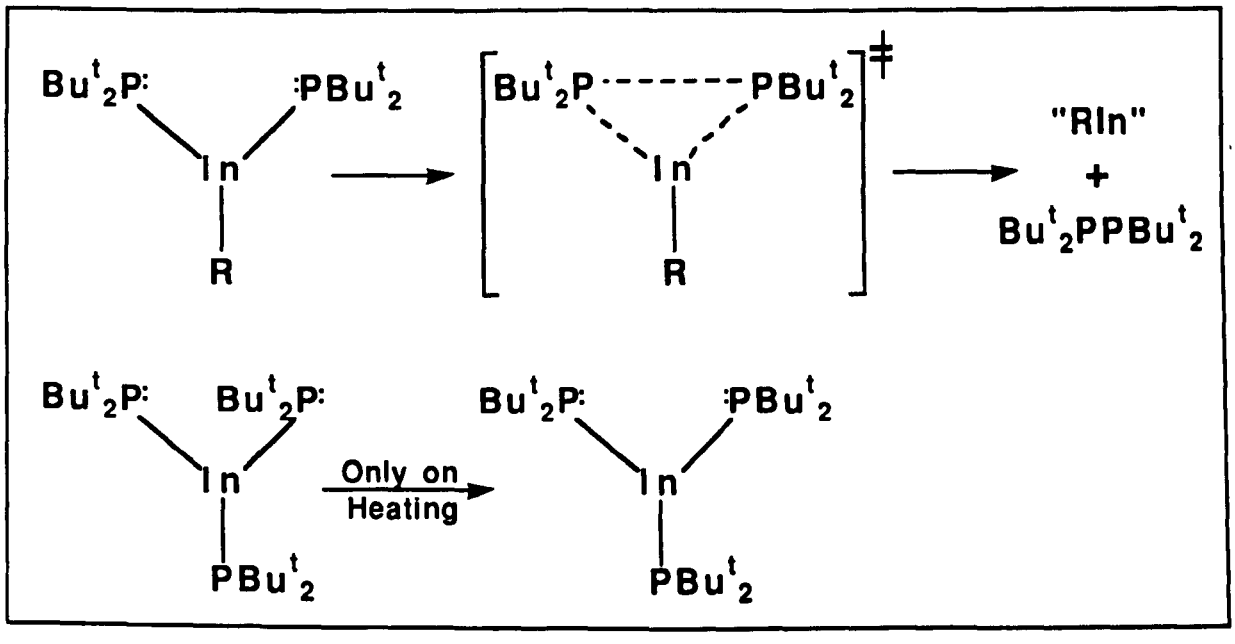


Diagram 4. Proposed mechanism for the formation of $Bu^t_2PPBu^t_2$.

Clearly, this mechanism would be favoured by compounds in which the phosphorus lone pairs are facing each other, ready to form the transition state shown in Diagram 4. This conformation would be sterically the most favourable in compounds of the type $RIn(PBu^t_2)_2$ and so this mechanism agrees with the observation that these compounds are unstable. However, for $In(PBu^t_2)_3$ the sterically most favoured conformation would have the phosphorus lone pairs all facing in the same direction around the indium atom. This was the structure found in the *X*-ray crystallographic study already described (see Chapter 4, page 116). In this case the compound cannot form the proposed

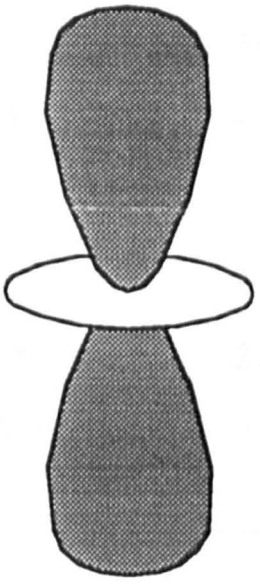
decomposition transition state unless enough energy (e.g., heat) is added to overcome the steric barrier to rotation of the In-P bond which arises from the steric bulk of the *t*-butyl groups. This mechanism, therefore, agrees with the observation that $In(PBu^t_2)_3$ decomposes to give only the biphosphine on heating.

The reaction scheme proposed for the thermal decomposition of $(Et_2InPBu^t_2)_2$ has great significance on any attempts to prepare indium phosphide (InP) from such precursors. The formation of $Bu^t_2PPBu^t_2$ during the reaction must lead to phosphorus deficiency in the indium phosphide. This is confirmed by the analysis of the black material that remained after the decomposition was complete. This material contained only 1% carbon showing that most of the organo groups had been eliminated. However, the material contained only 7.46 % phosphorus instead of the 21.3 % expected for indium phosphide. This confirmed the predicted result that phosphorus deficient indium phosphide would be formed.

Clearly, there is an inherent problem in the use of R_2PInR_2 type compounds as precursors in the preparation of indium phosphide. Attempts at preparing indium phosphide from such precursors, would therefore need to find a method of overcoming this problem either physically (varying experimental conditions) or chemically (changing the organo groups).

APPENDIX A

INDIUM-PHOSPHORUS BOND LENGTHS



During the course of this work it has been possible to carry out several single-crystal *X*-ray diffraction studies on compounds of indium that also contain phosphorus. This has greatly increased the number of known indium-phosphorus bond lengths and it is consequently possible to make some observations concerning the different values that are now available. The mean values of indium-phosphorus bond lengths that have been determined during the course of this work and those which have previously been reported are given in Table 1.

Compound	Mean In-P Bond Length (Å)
$Cl_3In(PMe_3)_2$	2.576(3)
$I_3In.HPPh_2$	2.599(9)
$I_3In.HPBu^t_2$	2.586(6)
$I_3In(Diphos)_{1.5}$	2.810(3)
$In(PBu^t_2)_3$	2.588(14)
$(Et_2InPBu^t_2)_2$	2.635(2)
$(Me_2InPBu^t_2)_2$ [84]	2.647(4)
$InCl_3(PPh_3)_2$ [38]	2.712
$[(Me_3SiCH_2)_2InPPh_2]_2$ [55]	2.650(2)
$[Li(THF)_4][In(PPh_2)_4]$ [128]	2.576(2)

Table 1. Indium-phosphorus bond lengths that have been determined by single-crystal *X*-ray diffraction studies.

The two longest bonds are found for complexes with a trigonal-bipyramidal structure. The diphos adduct of indium triiodide has a mean In-P length of 2.810(3) Å and the triphenylphosphine adduct, $InCl_3(PPh_3)_2$, has a value of 2.712 Å. This result can be rationalised in terms of steric crowding around the indium (both have five ligands bonded to the indium) as well as the steric bulk of the phenyl groups attached to the phosphorus. That the diphos adduct, $I_3In(Diphos)_{1.5}$, has a mean In-P bond length approximately 0.1 Å longer than that found in the triphenylphosphine adduct, $Cl_3In(PPh_3)_2$, is consistent with the larger size of the iodide ligands (with respect to chloride ligands) increasing the steric crowding around the indium atom and so lengthening the bonds to the axial ligands.

However, the trimethyl phosphine complex, $InCl_3(PMe_3)_2$, which is also trigonal-bipyramidal in structure, has the shortest In-P bond length of (mean) 2.576 Å. The difference in In-P bond lengths, between this complex and the other two, can be related to the strength of the phosphine ligand. Trimethylphosphine is a much more basic ligand than either triphenylphosphine or Diphos and so would be expected to form stronger donor-acceptor bonds with the indium trihalides. It appears, therefore, that the nature of the ligand is an important factor in determining the length of the In-P bond.

A bonding model that has been proposed for these trigonal bipyramidal indium complexes involves a set of sp^2 hybrid orbitals on the indium atom in the bonding with the equatorial halides and the $5p_z$ orbital on the indium bonding with the two axial ligands. (Throughout the following discussion the axis joining together the two axial ligands and the indium atom will be defined as the z-axis) The involvement of the indium $5d_z2$ orbital contributing to the bonding with the axial

ligands has also been suggested, although there is no evidence to substantiate this suggestion.[2,39]

A similar situation exists for the compound PF_5. This compound also has a trigonal bipyramidal structure and the contribution of the different phosphorus orbitals to the bonding in this molecule has also been discussed. Calculations have shown that the involvement of the 3*d* orbitals in the bonding leads to a small degree of stabilisation. Of the 3*d* orbitals available it was shown that only the $3d_z2$ orbital can lay claim to playing any significant part in the bonding, and then only to a small extent. The calculations also demonstrated that the same degree of stabilisation could be attained by including the phosphorus 4*s* orbital in the bonding scheme instead of the $3d_z2$.[149]

It is conceivable that such a situation could occur for these indium trihalide complexes. That is, that a contribution to the bonding of the ligands could come from both the $5d_z2$ and/or the 6*s* orbitals.

Using the conventional linear combination of atomic orbitals approach we can construct two group orbitals from the two phosphorus σ-orbitals to be used in the bonding scheme. These are the two combinations $(\sigma_1 + \sigma_2)$ and $(\sigma_1 - \sigma_2)$ which are represented in Diagram 1.

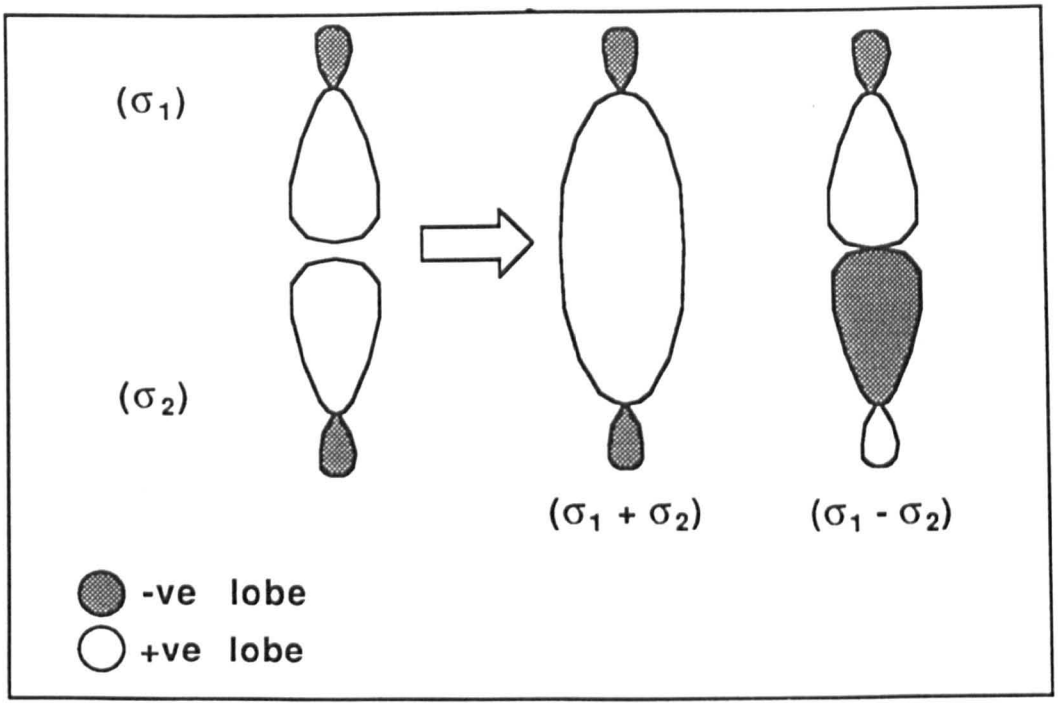
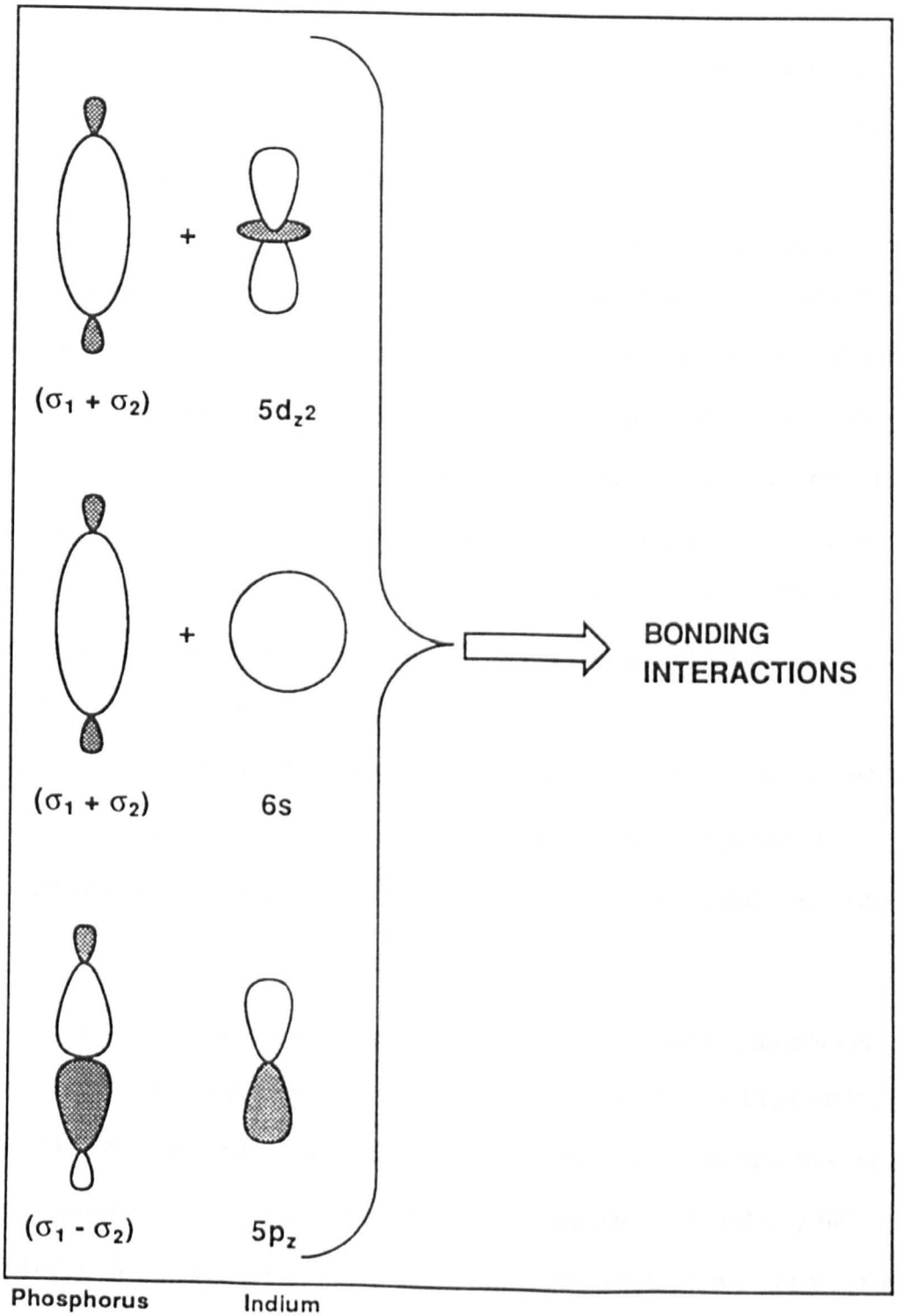


Diagram 1. Representation of the LCAO of the two σ-orbitals of the phosphorus atoms to create two group orbitals.

Having created two group orbitals to represent the contribution to the bonding from the axial phosphorus atoms, the interactions between these and the indium orbitals can be considered. It can be seen in Diagram 2 that the group orbital ($\sigma_1 + \sigma_2$) has the correct symmetry to give a bonding interaction with the indium $5d_z2$ and $6s$ orbitals. The other group orbital ($\sigma_1 - \sigma_2$) has the correct symmetry to give a bonding interaction only with the indium $5p_z$ orbital.

Diagram 2. Bonding interactions between the phosphorus group orbitals and the indium orbitals.



Phosphorus group orbitals.

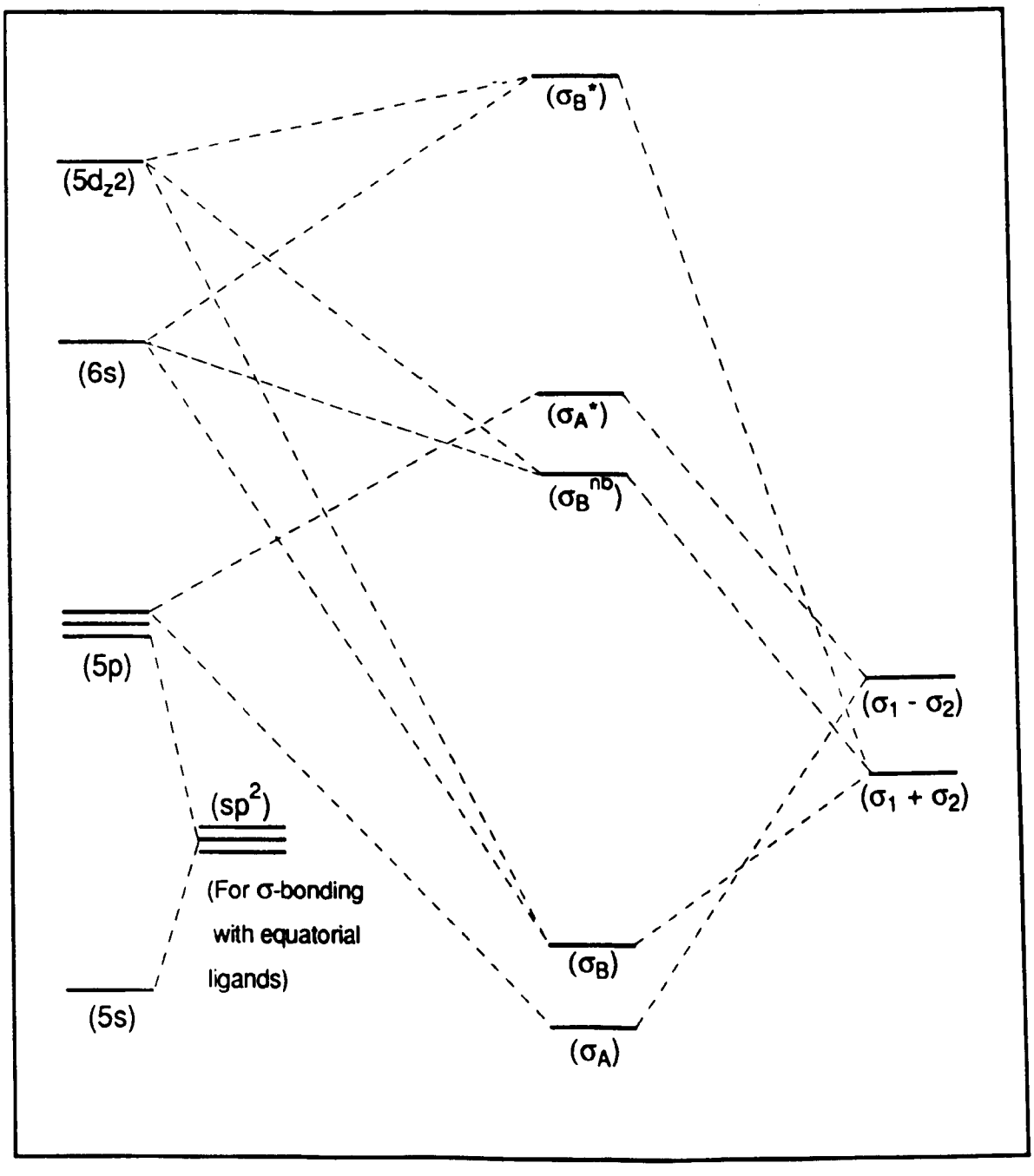
Indium orbitals.

Having deduced these bonding interactions from a qualitative consideration of the symmetry of the indium orbitals and the phosphorus group orbitals it is possible to represent these on a simplified (excluding the halides) combined orbital energy level diagram. This is shown in Diagram 3. It should be noted that this diagram is purely qualitative and so the relative positions of the orbitals on the diagram may not be representative of their actual energies. From this diagram we can see that two bonding combinations (σ_A and σ_B) are available to bind the axial ligands. Of these σ_A involves the ($\sigma_1 - \sigma_2$) group orbital and the $5p_z$ indium orbital and σ_B involves the ($\sigma_1 + \sigma_2$) group orbital with contributions from the indium $5d_z2$ and $6s$ orbitals. Whereas in reality these orbitals cannot be considered in isolation from the interactions ($\sigma + \pi$) involving the three halides, this simplified approach does give an indication of which metal orbitals can participate in the bonding with the axial ligands.

A more detailed picture of the bonding ($\sigma + \pi$) in these complexes can be derived from a rigorous molecular orbital approach taking into consideration the orbitals of all five of the ligands around the indium.

Three of the compounds listed in Table 1 have phosphorus atoms that are bridging between two indium atoms, ($[Et_2InPBu^t_2]_2$, $[Me_2InPBu^t_2]_2$ and $[(Me_3SiCH_2)_2InPPh_2]_2$). These compounds all have very similar values for their In-P bond lengths, 2.635(2), 2.647(4) and 2.650(2) Å respectively. All of these compounds have very sterically hindered substituents which is likely to lead to a small increase in the In-P bond length. It would appear that a value of approximately 2.63 - 2.64 Å is the "normal" value for this bond length when the phosphorus atoms are acting in a bridging mode.

Diagram 3. Simplified Orbital Diagram (excluding the equatorial ligands) showing the orbital contributions from the indium to the bonding with the axial ligands for a trigonal-bipyramidal indium complex.

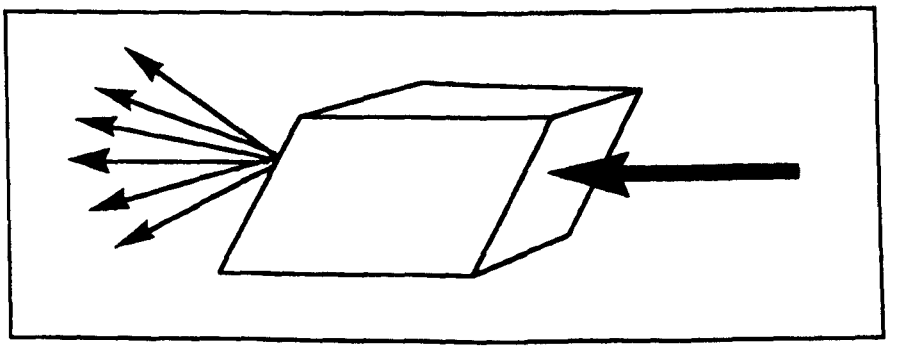


The remaining compounds listed in Table 1 all have shorter bond lengths than the compounds mentioned above and they all have similar values. $I_3In.HPBu^t_2$, $I_3In.HPPh_2$, $In(PBu^t_2)_3$ and the anion $[In(PPh_2)_4]^-$ have In-P bond lengths of 2.599(9), 2.586(6), 2.58(1) and 2.576(2) Å respectively. All of these compounds have sterically crowded indium atoms and so it is likely that these values are also slightly longer than a "normal" In-P single bond.

Comparisons of the mean values for In-C bond lengths (2.174 Å)[77,84] with the covalent radii of phosphorus and carbon (1.10 and 0.77 Å respectively)[150] give a predicted "normal" In-P bond length of 2.50 Å. This value is consistent with the values found for the compounds mentioned above with the shortest In-P bond lengths (which should be slightly longer due to steric crowding).

APPENDIX B

X-RAY CRYSTALLOGRAPHIC STUDIES



The *X*-ray crystallographic studies described for the compounds in this work were (with the exception of that for $[Et_2InPBu^t_2]_2$) carried out by the author with the help and expert guidance of Dr. N. W. Alcock and S. M. Roe. For the study of $In(PBu^t_2)_3$ the help of Prof. G. M. Sheldrick and Dr. H. R. Powell was also obtained.

General Method.

All of the crystals used were mounted under argon in thin walled quartz Lindemann tubes and held in place with a trace of silicon grease. The ends of the Lindemann tubes were heat sealed and further protected with wax. The air sensitive crystals were mounted in an argon-filled glove box fitted with a microscope. The less sensitive crystals were placed in the Lindemann tubes with a glass fibre. The Lindemann tubes were flushed with argon before this procedure.

The diffraction data for Compounds 1-5 (see Table 1) were collected at ambient temperature on a Nicolet R3M diffractometer in the ω-2θ mode. Three standard reflections were monitored after every 200 reflections and the data were rescaled to correct for any decrease in intensity of these standards that occurred during the collection. Unit cell dimensions and standard deviations were obtained by least squares fit to 15 high angle reflections. For the data collection, reflections with intensities $I/\sigma(I) > 2.0$ were considered observed and used in the structure refinement. They were corrected for Lorentz polarisation and absorption effects using the Gaussian method. The structure refinement of each compound is described individually below. Final refinement in each case was by least squares methods. A weighting scheme of the form $W = 1/(\sigma^2(F) + gF^2)$ was used and shown to be satisfactory by weight analysis. Computing work was carried out with SHELXTL PLUS [151] using

a DEC Microvax II. Scattering factors and anomolous dispersion factors were taken from the literature.[152]

The data for Compound 6 were collected on a Nicolet $P2_1$ four circle diffractometer, and for Compound 7 on a Phillips PW1100 diffractometer.

The unit cell data and the data collection parameters for all of the compounds are given below.

Compound Number	1	2
Compound	$InCl_3(PMe_3)_2$	$I_3In.HPBu^t_2$
Formula	$C_6H_{18}P_2Cl_3In$	$C_{16}H_{19}PInI_3$
Mol.Weight.	342.4	641.5
System	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma
a,(Å)	10.418(8)	9.411(6)
b,(Å)	10.769(9)	12.479(8)
c,(Å)	13.808(9)	14.719(11)
α,(°)	90.00	90.00
β,(°)	90.00	90.00
γ,(°)	90.00	90.00
V,($Å^3$)	1549(2)	1729(2)
D_c,(g cm^{-3})	1.47	2.46
Z	4	4
μ(Mo-K_α),(cm^{-1})	21.9	67.15
F(000)	736	1160
Total reflections.	1597	1774
Total reflections-	1247	1165
with $I/\sigma(I)>$	2.0	2.0
Max 2θ,(°)	50	50
2θ Range	-0.5,+0.6	-0.5,+0.6
Max. and min. transmission Factors	0.9691,0.9567	0.4064,0.1982
Crystal size,(mm)	0.3×0.5×0.2	0.5×0.5×0.2
g	0.00096	0.00062
R	0.0428	0.0815
R_w	0.0499	0.0932
Shift error	0.001	0.12

Compound Number	3	4
Compound	$(InI_3)_2(Diphos)_3$	$Me_2In(Sal)$
Formula	$C_{78}H_{72}P_6In_2I_6$	$C_9H_{11}O_2In$
Mol.Weight.	1194.7	265.9
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a,(Å)	12.583(7)	9.322(6)
b,(Å)	12.667(8)	7.006(4)
c,(Å)	13.080(8)	15.266(9)
α,(°)	76.59(4)	90.00
β,(°)	86.72(4)	100.03
γ,(°)	79.34(4)	90.00
V,(Å^3)	1993(2)	982(1)
D_c,(g cm^{-3})	0.99	1.80
Z	1	4
μ(Mo-K_α),(cm^{-1})	30.3	23.3
F(000)	1046	520
Total reflections.	6998	1734
Total reflections-	5203	1485
with I/σ(I)>	2.0	2.0
Max 2θ,(°)	50	50
2θ Range	-0.5,+0.6	-0.5,+0.6
Max. and min. transmission Factors	0.9691,0.9567	0.759,0.520
Crystal size,(mm)	0.4x0.4x0.4	0.4x0.3x0.4
g	0.010556	0.00054
R	0.0664	0.0270
R_w	0.0778	0.0309
Shift error	0.03	0.002

Compound Number	5	6
Compound	$InI_3(HPPh_2)$	$In(PBu^t_2)_3$
Formula	$C_{12}H_{11}PInI_3$	$C_{24}H_{54}P_3In$
Mol.Weight.	681.5	550.4
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	Cc
a,(Å)	12.454(9)	17.855(5)
b,(Å)	12.773(18)	30.873(8)
c,(Å)	14.158(12)	17.617(5)
α,(°)	102.58(9)	90.00
β,(°)	107.48(6)	111.66(2)
γ,(°)	114.69(10)	90.00
V,(Å^3)	1792(3)	9025(4)
D_c,(g cm^{-3})	2.53	1.22
Z	4	12
μ(Mo-K$_\alpha$),(cm^{-1})	23.3	9.3
F(000)	1224	2680
Total reflections.	4692	
Total reflections-	3304	3346
with I/σ(I)>	2.0	2.5
Max 2θ,(deg.)	45	45
2θ Range	-0.5,+0.55	-0.6,+0.6
Max. and min. transmission Factors	0.549,0.309	0.9365,0.753
Crystal size,(mm)	0.3×0.2×0.2	0.3×0.3×0.2
g	0.0759	0.000800
R	0.0703	0.1005
R_w	0.0755	0.0841
Shift error	0.02	0.486

Compound Number	7
Compound	$[Et_2InPBu^t_2]_2$
Formula	$C_{24}H_{56}P_2In_2$
Mol.Weight.	636.3
System	Monoclinic
Space group	I2/m
a,(Å)	14.869(3)
b,(Å)	11.605(2)
c,(Å)	9.003(2)
α,(°)	90.00
β,(°)	91.38(2)
γ,(°)	90.00
V,($Å^3$)	1553
D_c,(g cm^{-3})	1.36
Z	2
μ(Mo-K_α),(cm^{-1})	14.66
F(000)	656
Total reflections-	858
with $I/\sigma(I)>$	3.0
Max 2θ,(°)	50
2θ Range	-0.8,+0.8
R	0.0413
R_w	0.0417

Compound 1,[InCl$_3$(PMe$_3$)$_2$],

The data for this compound had systematic absences in hk0 (when h=odd) and 0kl (when k+l=odd). These indicated that the space group was either *Pn2$_1$a* or *Pnma*. The refinement converged better using *Pnma* and so this was chosen as the space group. The heavy atoms (In) were located using the Patterson interpretation section of SHELXTL[151] and the light atoms (C,P,Cl) were located by successive Fourier syntheses. Anisotropic temperature factors were used for all non-hydrogen atoms. Final refinement was on F by least squares methods refining 64 parameters.

The bond lengths and angles are given in Tables 1 and 2. The atomic co-ordinates of the non-hydrogen atoms are given in Table 3. The molecule was found to have crystallographic mirror symmetry. The atoms Cl(1A), C(22A) and C(12A) were generated by reflection across the mirror plane.

Table 1. Bond lengths for compound 1, (Å).

In(1)-Cl(1)	2.505 (3)	In(1)-Cl(2)	2.450 (4)
In(1)-P(1)	2.575 (3)	In(1)-P(2)	2.576 (3)
In(1)-Cl(1A)	2.505 (3)	P(1)-C(11)	1.789 (10)
P(1)-C(12)	1.779 (9)	P(1)-C(12A)	1.779 (9)
P(2)-C(21)	1.849 (12)	P(2)-C(22)	1.784 (8)
P(2)-C(22A)	1.784 (8)		

Table 2. Bond angles for compound 1, (°).

Cl(1)-In(1)-Cl(2)	121.9(1)	Cl(1)-In(1)-P(1)	90.2(1)
Cl(2)-In(1)-P(1)	87.8(1)	Cl(1)-In(1)-P(2)	92.1(1)
Cl(2)-In(1)-P(2)	87.9(1)	P(1)-In(1)-P(2)	175.7(1)
Cl(1)-In(1)-Cl(1A)	116.1(1)	Cl(2)-In(1)-Cl(1A)	121.9(1)
P(1)-In(1)-Cl(1A)	90.2(1)	P(2)-In(1)-Cl(1A)	92.1(1)
In(1)-P(1)-C(11)	112.2(4)	In(1)-P(1)-C(12)	113.6(3)
C(11)-P(1)-C(12)	104.8(4)	In(1)-P(1)-C(12A)	113.6(3)
C(11)-P(1)-C(12A)	104.8(4)	C(12)-P(1)-C(12A)	107.0(5)
In(1)-P(2)-C(21)	114.9(4)	In(1)-P(2)-C(22)	111.6(3)
C(21)-P(2)-C(22)	104.8(4)	In(1)-P(2)-C(22A)	111.6(3)
C(21)-P(2)-C(22A)	104.8(4)	C(22)-P(2)-C(22A)	108.6(5)

Table 3. Atomic co-ordinates for compound 1.

Atomic co-ordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x10^3$)

	x	y	z	U(eq)
In(1)	2093.9(5)	7500	5229.5(4)	44.3(2)
Cl(1)	2845(1)	5526(2)	6004(1)	59(1)
Cl(2)	644(3)	7500	3833(2)	88(1)
P(1)	90(2)	7500	6321(2)	53(1)
P(2)	3985(3)	7500	4028(2)	59(1)
C(11)	495(11)	7500	7580(7)	79(4)
C(12)	-905(7)	6172(8)	6165(7)	95(3)
C(21)	5593(11)	7500	4592(10)	82(4)
C(22)	3966(9)	8845(8)	3274(6)	88(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Compound 2. ($I_3In.HPBu^t_2$)

The data for this compound had systematic absences in h0l (when h+l=2n+1) and 0kl (when k=2n+1). These indicated that the space group was either *Pbnm* (n.s.s. of *Pnma*) or *Pbn2₁* (n.s.s. of *Pna2₁*). The refinement converged better using Pnma and so this was chosen as the space group. The heavy atoms (In,I) were located using the Patterson interpretation section of SHELXTL[151] and the light atoms (C,P) were located by successive Fourier syntheses. Anisotropic temperature factors were used for all non-hydrogen atoms. Final refinement was on F by least squares methods refining 65 parameters.

The bond lengths and angles are given in Tables 4 and 5. The atomic co-ordinates of the non-hydrogen atoms are given in Table 6. The molecule was found to have crystallographic mirror symmetry. One of the *t*-butyl groups and I(1a) were generated by reflection across the mirror plane.

Table 4. Bond lengths for compound 2, (Å).

In-I(1)	2.668(2)	In-I(2)	2.679(3)
In-P(1)	2.586(6)	In-I(1a)	2.667(2)
P(1)-C(1)	1.870(25)	P(1)-C(1a)	1.870(25)
C(1)-C(2)	1.517(39)	C(1)-C(3)	1.542(36)
C(1)-C(4)	1.570(47)		

Table 5. Bond angles for compound 2, (°).

I(1)-In-I(2)	107.7(1)	I(1)-In-P(1)	113.7(1)
I(2)-In-P(1)	106.7(1)	I(1)-In-I(1a)	107.0(1)
I(2)-In-I(1a)	107.7(1)	P(1)-In-I(1a)	113.7(1)
In-P(1)-C(1)	111.8(7)	In-P(1)-C(1a)	111.8(7)
C(1)-P(1)-C(1a)	119.1(14)	P(1)-C(1)-C(2)	104.3(17)
P(1)-C(1)-C(3)	112.9(18)	C(2)-C(1)-C(3)	106.8(25)
P(1)-C(1)-C(4)	106.1(22)	C(2)-C(1)-C(4)	116.7(30)
C(3)-C(1)-C(4)	110.1(23)		

Table 6. Atomic co-ordinates for compound 2.

Atom	x	y	z	U
In	316.4(14)	2500.0	2147.4(16)	50(1)*
I(1)	420.8(21)	1043.3(13)	3827.9(18)	120(1)*
I(2)	-1611(2)	2500	895(2)	184(2)*
P(1)	1724(5)	2500	131(6)	42(2)*
C(1)	1722(19)	1404(18)	-875(23)	91(9)*
C(2)	1906(40)	685(15)	253(39)	191(21)*
C(3)	2659(24)	1329(19)	-1935(26)	116(12)*
C(4)	625(30)	1368(34)	-1689(51)	240(27)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom co-ordinates ($x10^4$) and temperature factors (A^2x10^3)

Compound 3. $(InI_3)_2(Diphos)_3$.

No reflections were systematically absent indicating that the space group was $P\bar{1}$. The structure was solved using direct methods using SHELXTL/MULTAN 80.[151] The light atoms (C,P) were then located by successive Fourier syntheses. Anisotropic temperature factors were used for all non-hydrogen atoms. Final refinement was on F by least squares methods refining 415 parameters.

The bond lengths and angles are given in Tables 7 and 8. The atomic co-ordinates of the non-hydrogen atoms are given in Table 9.

Table 7. Bond lengths for compound 3, (Å).

In(1)-I(1)	2.742 (2)	In(1)-I(2)	2.739 (2)
In(1)-I(3)	2.713 (2)	In(1)-P(2)	2.798 (3)
In(1)-P(3)	2.821 (3)	P(1)-C(2)	1.846 (11)
P(1)-C(11)	1.815 (10)	P(1)-C(21)	1.816 (9)
P(2)-C(1)	1.828 (10)	P(2)-C(31)	1.818 (9)
P(2)-C(41)	1.828 (8)	P(3)-C(3)	1.844 (8)
P(3)-C(51)	1.824 (10)	P(3)-C(61)	1.803 (9)
C(1)-C(2)	1.558 (12)	C(3)-C(3A)	1.524 (17)
C(11)-C(12)	1.387 (16)	C(11)-C(16)	1.396 (17)
C(12)-C(13)	1.348 (18)	C(13)-C(14)	1.387 (28)
C(14)-C(15)	1.330 (23)	C(15)-C(16)	1.380 (19)
C(21)-C(22)	1.376 (15)	C(21)-C(26)	1.418 (13)
C(22)-C(23)	1.371 (19)	C(23)-C(24)	1.347 (26)
C(24)-C(25)	1.356 (24)	C(25)-C(26)	1.377 (19)
C(31)-C(32)	1.398 (13)	C(31)-C(36)	1.366 (12)
C(32)-C(33)	1.383 (17)	C(33)-C(34)	1.356 (18)
C(34)-C(35)	1.390 (17)	C(35)-C(36)	1.408 (15)
C(41)-C(42)	1.343 (15)	C(41)-C(46)	1.398 (13)
C(42)-C(43)	1.394 (14)	C(43)-C(44)	1.339 (16)
C(44)-C(45)	1.360 (18)	C(45)-C(46)	1.377 (13)
C(51)-C(52)	1.364 (13)	C(51)-C(56)	1.368 (12)
C(52)-C(53)	1.405 (17)	C(53)-C(54)	1.364 (16)
C(54)-C(55)	1.340 (15)	C(55)-C(56)	1.380 (17)
C(61)-C(62)	1.385 (13)	C(61)-C(66)	1.388 (16)
C(62)-C(63)	1.404 (15)	C(63)-C(64)	1.341 (22)
C(64)-C(65)	1.377 (18)	C(65)-C(66)	1.370 (16)

Table 8. Bond angles for compound 3, (°).

I(1)-In(1)-I(2)	119.7(1)	I(1)-In(1)-I(3)	119.9(1)
I(2)-In(1)-I(3)	120.4(1)	I(1)-In(1)-P(2)	91.9(1)
I(2)-In(1)-P(2)	89.5(1)	I(3)-In(1)-P(2)	89.7(1)
I(1)-In(1)-P(3)	92.3(1)	I(2)-In(1)-P(3)	84.4(1)
I(3)-In(1)-P(3)	92.3(1)	P(2)-In(1)-P(3)	173.8(1)
C(2)-P(1)-C(11)	98.2(5)	C(2)-P(1)-C(21)	101.3(5)
C(11)-P(1)-C(21)	102.6(4)	In(1)-P(2)-C(1)	113.5(3)
In(1)-P(2)-C(31)	113.0(3)	C(1)-P(2)-C(31)	103.6(4)
In(1)-P(2)-C(41)	115.4(3)	C(1)-P(2)-C(41)	105.0(4)
C(31)-P(2)-C(41)	105.4(4)	In(1)-P(3)-C(3)	114.5(3)
In(1)-P(3)-C(51)	117.0(2)	C(3)-P(3)-C(51)	106.5(4)
In(1)-P(3)-C(61)	111.5(3)	C(3)-P(3)-C(61)	102.4(4)
C(51)-P(3)-C(61)	103.4(4)	P(2)-C(1)-C(2)	110.3(6)
P(1)-C(2)-C(1)	112.4(6)	P(3)-C(3)-C(3A)	113.2(7)
P(1)-C(11)-C(12)	124.2(9)	P(1)-C(11)-C(16)	119.6(9)
C(12)-C(11)-C(16)	116.0(10)	C(11)-C(12)-C(13)	122.3(14)
C(12)-C(13)-C(14)	120.1(14)	C(13)-C(14)-C(15)	119.6(14)
C(14)-C(15)-C(16)	120.9(15)	C(11)-C(16)-C(15)	121.1(13)
P(1)-C(21)-C(22)	120.0(7)	P(1)-C(21)-C(26)	122.6(8)
C(22)-C(21)-C(26)	117.0(9)	C(21)-C(22)-C(23)	120.1(12)
C(22)-C(23)-C(24)	121.6(13)	C(23)-C(24)-C(25)	121.2(15)
C(24)-C(25)-C(26)	118.3(13)	C(21)-C(26)-C(25)	121.7(11)
P(2)-C(31)-C(32)	118.2(7)	P(2)-C(31)-C(36)	123.0(7)
C(32)-C(31)-C(36)	118.9(8)	C(31)-C(32)-C(33)	119.8(9)
C(32)-C(33)-C(34)	120.9(10)	C(33)-C(34)-C(35)	120.8(12)
C(34)-C(35)-C(36)	118.0(10)	C(31)-C(36)-C(35)	121.5(9)
P(2)-C(41)-C(42)	119.7(7)	P(2)-C(41)-C(46)	120.9(7)
C(42)-C(41)-C(46)	119.5(8)	C(41)-C(42)-C(43)	121.6(10)
C(42)-C(43)-C(44)	118.4(12)	C(43)-C(44)-C(45)	121.4(10)
C(44)-C(45)-C(46)	120.7(10)	C(41)-C(46)-C(45)	118.3(10)
P(3)-C(51)-C(52)	121.3(7)	P(3)-C(51)-C(56)	118.6(7)
C(52)-C(51)-C(56)	119.9(10)	C(51)-C(52)-C(53)	119.2(9)
C(52)-C(53)-C(54)	119.6(10)	C(53)-C(54)-C(55)	120.8(11)
C(54)-C(55)-C(56)	120.1(10)	C(51)-C(56)-C(55)	120.4(9)
P(3)-C(61)-C(62)	123.3(8)	P(3)-C(61)-C(66)	119.1(7)
C(62)-C(61)-C(66)	117.6(9)	C(61)-C(62)-C(63)	120.5(11)
C(62)-C(63)-C(64)	121.0(11)	C(63)-C(64)-C(65)	118.8(12)
C(64)-C(65)-C(66)	121.6(13)	C(61)-C(66)-C(65)	120.6(10)

Table 9. Atomic co-ordinates for compound 3.

	x	y	z	U(eq)
In(1)	3246.0(5)	7921.1(5)	3470.6(4)	41.1(2)
I(1)	4634.9(5)	7143.1(5)	2011.6(4)	51.4(2)
I(2)	1793.4(5)	6674.2(5)	4522.9(5)	55.7(2)
I(3)	3344.8(6)	9900.3(5)	3889.5(6)	64.4(3)
P(1)	1013(2)	6178(2)	677(2)	48.7(8)
P(2)	1691(2)	8968(2)	1946(2)	39.0(7)
P(3)	4631(2)	6772(2)	5142(2)	37.6(6)
C(1)	924(7)	8025(7)	1574(7)	47(3)
C(2)	1707(7)	7013(7)	1313(8)	49(3)
C(3)	4730(7)	5262(6)	5440(7)	43(3)
C(11)	1948(9)	4880(8)	1037(8)	61(4)
C(12)	1634(12)	3869(9)	1439(9)	77(5)
C(13)	2350(16)	2915(11)	1639(14)	111(8)
C(14)	3439(16)	2918(13)	1412(13)	112(8)
C(15)	3777(11)	3870(13)	1035(14)	103(7)
C(16)	3053(11)	4852(12)	830(11)	87(5)
C(21)	-116(8)	5955(7)	1579(7)	51(3)
C(22)	-1155(9)	6199(10)	1207(10)	70(4)
C(23)	-2013(10)	6096(12)	1895(15)	99(7)
C(24)	-1873(13)	5791(13)	2943(15)	100(7)
C(25)	-871(13)	5549(11)	3360(10)	88(6)
C(26)	6(10)	5635(9)	2686(7)	65(4)
C(31)	652(7)	9974(7)	2387(6)	43(3)
C(32)	108(8)	9636(9)	3335(8)	67(4)
C(33)	-659(10)	10388(12)	3715(8)	83(5)
C(34)	-928(11)	11443(12)	3159(10)	89(6)
C(35)	-431(10)	11797(9)	2196(9)	75(4)
C(36)	384(8)	11040(8)	1835(8)	58(4)
C(41)	2213(7)	9708(6)	705(6)	41(3)
C(42)	3096(9)	10164(8)	704(7)	59(4)
C(43)	3487(10)	10785(10)	-214(8)	71(4)
C(44)	2989(10)	10883(9)	-1118(8)	66(4)
C(45)	2118(9)	10397(9)	-1150(7)	69(4)
C(46)	1695(8)	9821(8)	-242(7)	57(3)
C(51)	6015(7)	7034(7)	5050(6)	42(3)
C(52)	6759(9)	6476(9)	5792(8)	67(4)
C(53)	7796(9)	6752(10)	5721(10)	80(5)
C(54)	8039(8)	7577(10)	4918(9)	68(4)
C(55)	7298(9)	8132(11)	4199(8)	75(5)
C(56)	6276(9)	7870(8)	4263(8)	61(4)
C(61)	4136(7)	7109(7)	6369(6)	43(3)
C(62)	3575(9)	6444(8)	7115(8)	62(4)
C(63)	3196(9)	6763(11)	8048(8)	74(5)
C(64)	3372(11)	7711(12)	8240(10)	83(5)
C(65)	3918(10)	8381(10)	7497(9)	72(4)
C(66)	4301(8)	8090(9)	6581(8)	60(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atomic co-ordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x10^3$)

Compound 4. $Me_2In(Sal)$

The data for this compound showed systematic absences in h0l (when h+l=2n+1) and 0k0 (when k=2n+1). These indicated that the space group was $P2_1/n$. The heavy atoms (In) were located using the Patterson interpretation section of SHELXTL[151] and the light atoms (C,O) were located by successive Fourier syntheses. Anisotropic temperature factors were used for all non-hydrogen atoms. Final refinement was on F by least squares methods refining 110 parameters.

The bond lengths and angles are given in Tables 10 and 11. The atomic co-ordinates of the non-hydrogen atoms are given in Table 12. The molecule was found to be dimeric. The second half of the dimer was symmetry generated.

Table 10. Bond lengths for compound 4, (Å).

In(1)-O(1)	2.188 (3)	In(1)-O(2)	2.341 (4)
In(1)-C(1)	2.121 (5)	In(1)-C(2)	2.123 (6)
In(1)-O(1A)	2.383 (3)	O(1)-C(3)	1.325 (5)
O(1)-In(1A)	2.383 (3)	O(2)-C(9)	1.214 (5)
C(3)-C(4)	1.394 (5)	C(3)-C(8)	1.404 (6)
C(4)-C(5)	1.381 (6)	C(5)-C(6)	1.368 (7)
C(6)-C(7)	1.374 (6)	C(7)-C(8)	1.404 (5)
C(8)-C(9)	1.425 (6)		

Table 11. Bond angles for compound 4, (°).

O(1)-In(1)-O(2)	79.9(1)	O(1)-In(1)-C(1)	109.0(2)
O(2)-In(1)-C(1)	91.7(2)	O(1)-In(1)-C(2)	109.1(2)
O(2)-In(1)-C(2)	96.1(2)	C(1)-In(1)-C(2)	141.9(2)
O(1)-In(1)-O(1A)	74.8(1)	O(2)-In(1)-O(1A)	154.7(1)
C(1)-In(1)-O(1A)	94.5(2)	C(2)-In(1)-O(1A)	94.1(2)
In(1)-O(1)-C(3)	133.7(3)	In(1)-O(1)-In(1A)	105.2(1)
C(3)-O(1)-In(1A)	121.1(2)	In(1)-O(2)-C(9)	128.2(3)
O(1)-C(3)-C(4)	119.3(4)	O(1)-C(3)-C(8)	123.2(3)
C(4)-C(3)-C(8)	117.6(3)	C(3)-C(4)-C(5)	121.5(4)
C(4)-C(5)-C(6)	121.3(4)	C(5)-C(6)-C(7)	118.5(4)
C(6)-C(7)-C(8)	121.7(4)	C(3)-C(8)-C(7)	119.5(3)
C(3)-C(8)-C(9)	126.0(3)	C(7)-C(8)-C(9)	114.6(4)
O(2)-C(9)-C(8)	128.5(4)		

Table 12. Atomic co-ordinates for compound 4.

	x	y	z	U(eq)
In(1)	10077.6(3)	1224.8(4)	11056.2(2)	48.3(2)
O(1)	8580(3)	686(5)	9809(2)	52(1)
O(2)	7995(4)	2783(5)	11356(2)	70(1)
C(1)	9851(6)	-985(7)	11972(3)	74(2)
C(2)	11290(6)	3739(7)	10919(4)	76(2)
C(3)	7207(4)	1159(5)	9507(3)	44(1)
C(4)	6572(5)	635(7)	8646(3)	56(1)
C(5)	5135(5)	1055(7)	8307(3)	62(2)
C(6)	4285(5)	2038(7)	8798(3)	62(2)
C(7)	4879(4)	2557(6)	9652(3)	57(2)
C(8)	6338(4)	2160(5)	10016(2)	44(1)
C(9)	6788(5)	2829(7)	10903(3)	57(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atomic co-ordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x10^3$)

Compound 5. ($I_3In.HPPh_2$)

No reflections were systematically absent indicating that the space group was $P\bar{1}$. This was confirmed by a density calculation. The structure was solved using direct methods using SHELXTL/MULTAN 80.[151] The light atoms (C,P) were located by successive Fourier syntheses. Anisotropic temperature factors were used for all non-hydrogen atoms. Final refinement was on F by least squares methods refining 307 parameters.

Two different molecules were located in the unit cell. The bond lengths and angles for these are given in Tables 13 and 14. The atomic co-ordinates of the non-hydrogen atoms are given in Table 15.

Table 13. Bond lengths for compound 5, (Å).

In(1)-I(1)	2.674 (5)	In(1)-I(2)	2.676 (5)
In(1)-I(3)	2.672 (5)	In(1)-P(1)	2.605 (9)
In(2)-I(4)	2.674 (4)	In(2)-I(5)	2.665 (5)
In(2)-I(6)	2.676 (5)	In(2)-P(2)	2.592 (9)
P(1)-C(1)	1.800 (26)	P(1)-C(7)	1.813 (20)
P(2)-C(13)	1.785 (27)	P(2)-C(19)	1.812 (30)
C(1)-C(2)	1.397 (41)	C(1)-C(6)	1.401 (37)
C(2)-C(3)	1.348 (43)	C(3)-C(4)	1.364 (49)
C(4)-C(5)	1.403 (54)	C(5)-C(6)	1.361 (45)
C(7)-C(8)	1.363 (38)	C(7)-C(12)	1.371 (41)
C(8)-C(9)	1.351 (37)	C(9)-C(10)	1.290 (55)
C(10)-C(11)	1.386 (48)	C(11)-C(12)	1.394 (33)
C(13)-C(14)	1.354 (39)	C(13)-C(18)	1.394 (31)
C(14)-C(15)	1.412 (51)	C(15)-C(16)	1.338 (44)
C(16)-C(17)	1.447 (51)	C(17)-C(18)	1.370 (48)
C(19)-C(20)	1.405 (26)	C(19)-C(24)	1.371 (37)
C(20)-C(21)	1.418 (52)	C(21)-C(22)	1.346 (50)
C(22)-C(23)	1.330 (35)	C(23)-C(24)	1.440 (50)

Table 14. Bond angles for compound 5, (°).

I(1)-In(1)-I(2)	114.3(1)	I(1)-In(1)-I(3)	114.3(1)
I(2)-In(1)-I(3)	113.1(1)	I(1)-In(1)-P(1)	102.8(2)
I(2)-In(1)-P(1)	108.1(2)	I(3)-In(1)-P(1)	102.8(2)
I(4)-In(2)-I(5)	113.0(1)	I(4)-In(2)-I(6)	114.3(1)
I(5)-In(2)-I(6)	113.5(1)	I(4)-In(2)-P(2)	103.7(2)
I(5)-In(2)-P(2)	111.8(2)	I(6)-In(2)-P(2)	99.3(2)
In(1)-P(1)-C(1)	113.4(8)	In(1)-P(1)-C(7)	113.0(11)
C(1)-P(1)-C(7)	109.5(12)	In(2)-P(2)-C(13)	116.9(10)
In(2)-P(2)-C(19)	111.8(9)	C(13)-P(2)-C(19)	109.5(13)
P(1)-C(1)-C(2)	123.1(20)	P(1)-C(1)-C(6)	117.8(20)
C(2)-C(1)-C(6)	119.2(24)	C(1)-C(2)-C(3)	120.7(28)
C(2)-C(3)-C(4)	122.0(33)	C(3)-C(4)-C(5)	116.8(31)
C(4)-C(5)-C(6)	123.4(29)	C(1)-C(6)-C(5)	117.7(26)
P(1)-C(7)-C(8)	119.5(22)	P(1)-C(7)-C(12)	120.3(18)
C(8)-C(7)-C(12)	120.2(21)	C(7)-C(8)-C(9)	121.2(31)
C(8)-C(9)-C(10)	120.0(31)	C(9)-C(10)-C(11)	122.0(25)
C(10)-C(11)-C(12)	119.2(31)	C(7)-C(12)-C(11)	117.5(26)
P(2)-C(13)-C(14)	122.8(18)	P(2)-C(13)-C(18)	118.7(21)
C(14)-C(13)-C(18)	118.5(25)	C(13)-C(14)-C(15)	120.9(23)
C(14)-C(15)-C(16)	120.7(35)	C(15)-C(16)-C(17)	119.6(35)
C(16)-C(17)-C(18)	117.8(24)	C(13)-C(18)-C(17)	122.3(29)
P(2)-C(19)-C(20)	119.0(21)	P(2)-C(19)-C(24)	120.0(17)
C(20)-C(19)-C(24)	120.9(28)	C(19)-C(20)-C(21)	118.6(24)
C(20)-C(21)-C(22)	118.8(24)	C(21)-C(22)-C(23)	122.5(40)
C(22)-C(23)-C(24)	120.4(30)	C(19)-C(24)-C(23)	117.5(20)

Table 15. Atomic co-ordinates for compound 5.

	x	y	z	U(eq)
In(1)	4885(2)	27(2)	8029(1)	50(1)
In(2)	3125(2)	3217(2)	3024(1)	49(1)
I(1)	4337(2)	129(2)	6087(1)	67(1)
I(2)	7425(2)	872(2)	9215(2)	80(1)
I(3)	3251(2)	-2165(2)	8007(2)	84(1)
I(4)	1163(2)	1827(2)	1029(1)	70(1)
I(5)	3558(2)	1841(2)	4088(2)	86(1)
I(6)	5320(2)	5037(2)	3140(1)	76(1)
P(1)	4285(6)	1545(5)	8974(4)	45(3)
P(2)	2366(6)	4579(6)	3937(4)	47(3)
C(1)	2740(22)	1329(19)	8130(16)	47(12)
C(2)	1613(26)	799(21)	8294(18)	61(15)
C(3)	486(25)	679(26)	7650(25)	81(17)
C(4)	367(34)	992(27)	6778(20)	78(20)
C(5)	1510(32)	1551(26)	6634(19)	78(20)
C(6)	2677(22)	1709(22)	7268(17)	50(14)
C(7)	5566(22)	3183(20)	9511(17)	49(13)
C(8)	5764(29)	4005(24)	10432(19)	70(18)
C(9)	6661(30)	5243(29)	10825(22)	83(20)
C(10)	7358(30)	5663(24)	10332(27)	87(19)
C(11)	7211(27)	4882(24)	9394(23)	66(18)
C(12)	6302(22)	3599(23)	8977(19)	56(14)
C(13)	1260(21)	3878(22)	4478(15)	43(13)
C(14)	1283(27)	4538(24)	5381(18)	67(16)
C(15)	339(32)	3960(37)	5744(23)	87(25)
C(16)	-574(30)	2736(31)	5224(24)	69(20)
C(17)	-570(30)	1990(26)	4297(22)	76(18)
C(18)	359(27)	2588(24)	3968(20)	70(17)
C(19)	1701(22)	5220(22)	3063(16)	49(14)
C(20)	440(23)	4426(23)	2194(18)	52(15)
C(21)	-58(30)	4929(31)	1497(24)	91(20)
C(22)	601(31)	6178(32)	1778(26)	83(22)
C(23)	1819(28)	6934(26)	2564(20)	63(17)
C(24)	2416(27)	6469(24)	3264(23)	70(17)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atomic co-ordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x10^3$)

Compound 6. $(In(PBu^t_2)_3$

The data for this compound showed systematic absences in h0l (when h or l=odd) and hkl (when h+k=odd). These indicated that the space group was *Cc* or *C/2c*. The heavy atoms (In) were located using the Patterson interpretation section of SHELXTL[151] and the light atoms (C,O) were located by successive Fourier syntheses. This structure was refined with considerable difficulty because of pseudo-symmetry (the heavy atoms were in *C2/c* with pseudo-threefold symmetry). This was resolved by using distant constraints. Anisotropic temperature factors were used for all non-hydrogen atoms. The bond lengths and angles are given in Tables 16 and 17. The atomic co-ordinates of the non-hydrogen atoms are given in Table 18.

Three different molecules were located in the unit cell. These are shown in Diagram 1 in which the staggered arrangement of the molecules can be seen.

Table 16. Bond lengths for compound 6, (Å).

In(1)-P(11)	2.588	(14)	In(1)-P(12)	2.574	(11)
In(1)-P(13)	2.613	(12)	P(11)-C(111)	1.954	(44)
P(11)-C(115)	1.744	(65)	C(111)-C(112)	1.779	(112)
C(111)-C(113)	1.528	(66)	C(111)-C(114)	1.341	(79)
C(115)-C(116)	1.467	(72)	C(115)-C(117)	1.737	(67)
C(115)-C(118)	1.502	(82)	P(12)-C(121)	2.061	(49)
P(12)-C(125)	1.964	(38)	C(121)-C(122)	1.585	(64)
C(121)-C(123)	1.541	(59)	C(121)-C(124)	1.599	(69)
C(125)-C(126)	1.421	(89)	C(125)-C(127)	1.460	(56)
C(125)-C(128)	1.619	(61)	P(13)-C(131)	1.761	(34)
P(13)-C(135)	2.080	(39)	C(131)-C(132)	1.574	(63)
C(131)-C(133)	1.538	(73)	C(131)-C(134)	1.470	(55)
C(135)-C(136)	1.455	(55)	C(135)-C(137)	1.630	(52)
C(135)-C(138)	1.636	(68)	In(2)-P(21)	2.583	(16)
In(2)-P(22)	2.588	(16)	In(2)-P(23)	2.625	(15)
P(21)-C(211)	1.818	(36)	P(21)-C(215)	1.450	(61)
C(211)-C(212)	1.711	(71)	C(211)-C(213)	1.631	(85)
C(211)-C(214)	1.539	(70)	C(215)-C(216)	1.671	(52)
C(215)-C(217)	1.527	(67)	C(215)-C(218)	1.788	(82)
P(22)-C(221)	1.908	(53)	P(22)-C(225)	1.719	(51)
C(221)-C(222)	1.592	(58)	C(221)-C(223)	1.623	(70)
C(221)-C(224)	1.523	(67)	C(225)-C(226)	1.344	(72)
C(225)-C(227)	1.464	(73)	C(225)-C(228)	1.769	(61)
P(23)-C(231)	1.683	(63)	P(23)-C(235)	2.098	(56)
C(231)-C(232)	1.555	(72)	C(231)-C(233)	1.587	(90)
C(231)-C(234)	1.618	(73)	C(235)-C(236)	1.453	(106)
C(235)-C(237)	1.467	(73)	C(235)-C(238)	1.735	(75)
In(3)-P(31)	2.558	(14)	In(3)-P(32)	2.614	(12)
In(3)-P(33)	2.547	(14)	P(31)-C(311)	1.954	(36)
P(31)-C(315)	1.868	(49)	C(311)-C(312)	1.621	(65)
C(311)-C(313)	1.456	(65)	C(311)-C(314)	1.529	(78)
C(315)-C(316)	1.405	(58)	C(315)-C(317)	1.559	(62)
C(315)-C(318)	1.476	(70)	P(32)-C(321)	1.904	(45)
P(32)-C(325)	1.986	(44)	C(321)-C(322)	1.296	(69)
C(321)-C(323)	1.564	(81)	C(321)-C(324)	1.646	(62)
C(325)-C(326)	1.390	(92)	C(325)-C(327)	1.448	(62)
C(325)-C(328)	1.607	(67)	P(33)-C(331)	1.590	(55)
P(33)-C(335)	2.086	(40)	C(331)-C(332)	1.624	(93)
C(331)-C(333)	1.603	(80)	C(331)-C(334)	1.439	(100)
C(335)-C(336)	1.493	(56)	C(335)-C(337)	1.585	(66)
C(335)-C(338)	1.544	(52)			

Table 17. Bond angles for compound 6, (°).

P(11)-In(1)-P(12)	120.7(4)	P(11)-In(1)-P(13)	120.4(4)
P(12)-In(1)-P(13)	118.8(4)	In(1)-P(11)-C(111)	103.6(16)
In(1)-P(11)-C(115)	106.0(19)	C(111)-P(11)-C(115)	105.4(23)
P(11)-C(111)-C(112)	106.2(34)	P(11)-C(111)-C(113)	108.9(35)
C(112)-C(111)-C(113)	102.8(40)	P(11)-C(111)-C(114)	129.8(33)
C(112)-C(111)-C(114)	90.6(51)	C(113)-C(111)-C(114)	112.8(41)
P(11)-C(115)-C(116)	104.8(41)	P(11)-C(115)-C(117)	121.6(42)
C(116)-C(115)-C(117)	103.3(36)	P(11)-C(115)-C(118)	112.6(35)
C(116)-C(115)-C(118)	110.1(54)	C(117)-C(115)-C(118)	103.8(41)
In(1)-P(12)-C(121)	102.9(11)	In(1)-P(12)-C(125)	103.4(13)
C(121)-P(12)-C(125)	113.4(18)	P(12)-C(121)-C(122)	106.4(38)
P(12)-C(121)-C(123)	110.3(29)	C(122)-C(121)-C(123)	108.7(36)
P(12)-C(121)-C(124)	113.7(32)	C(122)-C(121)-C(124)	98.5(37)
C(123)-C(121)-C(124)	117.9(39)	P(12)-C(125)-C(126)	100.2(29)
P(12)-C(125)-C(127)	110.3(28)	C(126)-C(125)-C(127)	127.9(42)
P(12)-C(125)-C(128)	101.8(26)	C(126)-C(125)-C(128)	111.4(39)
C(127)-C(125)-C(128)	102.5(35)	In(1)-P(13)-C(131)	105.6(13)
In(1)-P(13)-C(135)	98.3(11)	C(131)-P(13)-C(135)	109.9(17)
P(13)-C(131)-C(132)	107.8(25)	P(13)-C(131)-C(133)	111.5(28)
C(132)-C(131)-C(133)	107.5(43)	P(13)-C(131)-C(134)	120.2(31)
C(132)-C(131)-C(134)	105.9(28)	C(133)-C(131)-C(134)	103.3(35)
P(13)-C(135)-C(136)	104.1(29)	P(13)-C(135)-C(137)	108.7(21)
C(136)-C(135)-C(137)	122.9(38)	P(13)-C(135)-C(138)	97.9(34)
C(136)-C(135)-C(138)	116.3(33)	C(137)-C(135)-C(138)	104.0(31)
P(21)-In(2)-P(22)	120.4(5)	P(21)-In(2)-P(23)	121.4(6)
P(22)-In(2)-P(23)	118.2(5)	In(2)-P(21)-C(211)	102.0(15)
In(2)-P(21)-C(215)	109.9(20)	C(211)-P(21)-C(215)	103.4(24)
P(21)-C(211)-C(212)	114.8(29)	P(21)-C(211)-C(213)	139.2(38)
C(212)-C(211)-C(213)	78.2(46)	P(21)-C(211)-C(214)	113.4(31)
C(212)-C(211)-C(214)	88.8(39)	C(213)-C(211)-C(214)	105.0(41)
P(21)-C(215)-C(216)	111.0(35)	P(21)-C(215)-C(217)	130.3(36)
C(216)-C(215)-C(217)	103.9(35)	P(21)-C(215)-C(218)	129.4(38)
C(216)-C(215)-C(218)	89.2(32)	C(217)-C(215)-C(218)	83.9(36)
In(2)-P(22)-C(221)	99.8(15)	In(2)-P(22)-C(225)	106.8(20)
C(221)-P(22)-C(225)	114.9(23)	P(22)-C(221)-C(222)	108.0(31)
P(22)-C(221)-C(223)	113.3(39)	C(222)-C(221)-C(223)	114.0(33)
P(22)-C(221)-C(224)	113.4(27)	C(222)-C(221)-C(224)	104.1(40)
C(223)-C(221)-C(224)	103.7(38)	P(22)-C(225)-C(226)	112.7(34)
P(22)-C(225)-C(227)	112.0(44)	C(226)-C(225)-C(227)	112.9(39)
P(22)-C(225)-C(228)	109.8(27)	C(226)-C(225)-C(228)	110.2(45)
C(227)-C(225)-C(228)	98.2(35)	In(2)-P(23)-C(231)	106.1(20)
In(2)-P(23)-C(235)	101.8(16)	C(231)-P(23)-C(235)	113.9(25)
P(23)-C(231)-C(232)	102.3(39)	P(23)-C(231)-C(233)	133.4(35)
C(232)-C(231)-C(233)	86.6(44)	P(23)-C(231)-C(234)	112.0(46)
C(232)-C(231)-C(234)	92.3(38)	C(233)-C(231)-C(234)	113.1(47)
P(23)-C(235)-C(236)	109.5(40)	P(23)-C(235)-C(237)	99.2(32)
C(236)-C(235)-C(237)	120.5(64)	P(23)-C(235)-C(238)	103.7(35)
C(236)-C(235)-C(238)	107.4(46)	C(237)-C(235)-C(238)	114.9(43)
P(31)-In(3)-P(32)	118.9(4)	P(31)-In(3)-P(33)	122.1(5)
P(32)-In(3)-P(33)	119.0(5)	In(3)-P(31)-C(311)	109.6(14)
In(3)-P(31)-C(315)	106.3(15)	C(311)-P(31)-C(315)	110.6(18)
P(31)-C(311)-C(312)	101.7(24)	P(31)-C(311)-C(313)	111.0(33)
C(312)-C(311)-C(313)	114.5(31)	P(31)-C(311)-C(314)	117.6(27)
C(312)-C(311)-C(314)	93.6(40)	C(313)-C(311)-C(314)	116.3(38)
P(31)-C(315)-C(316)	107.8(34)	P(31)-C(315)-C(317)	112.9(36)
C(316)-C(315)-C(317)	97.5(33)	P(31)-C(315)-C(318)	117.9(28)

Table 17. Bond angles for compound 6, (°).(continued)

C(316)-C(315)-C(318)	119.2(48)	C(317)-C(315)-C(318)	99.3(35)
In(3)-P(32)-C(321)	99.4(11)	In(3)-P(32)-C(325)	100.6(15)
C(321)-P(32)-C(325)	119.9(20)	P(32)-C(321)-C(322)	110.9(50)
P(32)-C(321)-C(323)	109.0(35)	C(322)-C(321)-C(323)	109.8(50)
P(32)-C(321)-C(324)	115.2(30)	C(322)-C(321)-C(324)	109.5(45)
C(323)-C(321)-C(324)	102.0(39)	P(32)-C(325)-C(326)	98.0(31)
P(32)-C(325)-C(327)	108.8(31)	C(326)-C(325)-C(327)	127.1(46)
P(32)-C(325)-C(328)	97.3(29)	C(326)-C(325)-C(328)	119.7(42)
C(327)-C(325)-C(328)	101.3(39)	In(3)-P(33)-C(331)	105.7(22)
In(3)-P(33)-C(335)	101.4(10)	C(331)-P(33)-C(335)	108.5(29)
P(33)-C(331)-C(332)	106.4(41)	P(33)-C(331)-C(333)	118.0(38)
C(332)-C(331)-C(333)	96.6(48)	P(33)-C(331)-C(334)	126.0(60)
C(332)-C(331)-C(334)	105.6(49)	C(333)-C(331)-C(334)	99.9(48)
P(33)-C(335)-C(336)	102.6(29)	P(33)-C(335)-C(337)	111.0(26)
C(336)-C(335)-C(337)	111.4(38)	P(33)-C(335)-C(338)	101.0(28)
C(336)-C(335)-C(338)	117.7(29)	C(337)-C(335)-C(338)	112.0(32)

Table 18. Atomic co-ordinates for compound 6.

	x	y	z	U(eq)
In(1)	5000	3602(1)	2500	57(2)
P(11)	6492(7)	3581(4)	2632(8)	33(3)
C(111)	7006(26)	3209(14)	3580(28)	29(12)
C(112)	6864(50)	3469(26)	4418(54)	216(45)
C(113)	7919(28)	3230(16)	3814(34)	65(16)
C(114)	6759(35)	2831(20)	3781(38)	102(23)
C(115)	6509(33)	3285(18)	1795(35)	69(18)
C(116)	5984(32)	3526(17)	1079(34)	82(18)
C(117)	6134(24)	2761(13)	1607(26)	45(12)
C(118)	7341(27)	3247(15)	1776(29)	64(14)
P(12)	4184(7)	2898(3)	2339(8)	24(3)
C(121)	3795(22)	2926(12)	3304(23)	17(10)
C(122)	4566(38)	3031(19)	4091(43)	114(27)
C(123)	3453(26)	2484(13)	3424(27)	59(13)
C(124)	3280(33)	3350(17)	3302(36)	75(19)
C(125)	3311(23)	2965(12)	1269(26)	32(11)
C(126)	3737(34)	2879(19)	745(37)	104(21)
C(127)	2822(22)	3344(12)	1270(24)	31(10)
C(128)	2719(25)	2569(14)	1270(28)	48(13)
P(13)	4278(7)	4343(3)	2460(8)	32(3)
C(131)	4897(22)	4627(11)	3333(22)	24(10)
C(132)	4939(27)	4358(13)	4105(28)	52(13)
C(133)	4540(37)	5073(19)	3395(41)	117(25)
C(134)	5736(20)	4727(11)	3446(20)	29(9)
C(135)	4405(19)	4599(10)	1422(19)	8(8)
C(136)	3964(31)	4299(15)	775(31)	72(16)
C(137)	5350(22)	4721(13)	1639(24)	42(11)
C(138)	3975(37)	5068(19)	1419(43)	101(23)
In(2)	-22(2)	5263(1)	2459(3)	22(1)
P(21)	845(10)	4585(5)	2518(10)	53(4)
C(211)	1716(23)	4678(12)	3449(24)	31(11)
C(212)	1513(27)	4681(13)	4325(27)	45(13)
C(213)	2273(52)	5080(27)	3951(57)	224(49)
C(214)	2235(38)	4271(20)	3764(41)	108(25)
C(215)	1177(28)	4607(16)	1882(29)	51(14)
C(216)	452(22)	4693(11)	970(23)	20(10)
C(217)	1766(21)	4305(12)	1697(23)	27(9)
C(218)	1761(33)	5026(18)	1666(39)	75(19)
P(22)	-1531(8)	5185(4)	2239(9)	35(3)
C(221)	-1443(27)	4825(15)	3149(29)	40(13)
C(222)	-903(24)	5073(13)	3960(26)	33(11)
C(223)	-1136(32)	4338(16)	3073(34)	77(17)
C(224)	-2243(20)	4754(12)	3255(21)	28(9)
C(225)	-1995(28)	4947(15)	1300(32)	48(14)
C(226)	-1945(24)	5189(12)	686(25)	38(11)
C(227)	-2821(29)	4813(16)	1166(33)	60(15)
C(228)	-1578(22)	4427(12)	1294(25)	27(10)
P(23)	570(9)	6047(5)	2529(11)	47(4)
C(231)	402(30)	6300(15)	3297(32)	58(16)
C(232)	965(36)	6049(19)	4059(38)	94(23)
C(233)	-273(30)	6255(16)	3677(34)	79(17)
C(234)	928(36)	6739(18)	3574(41)	93(21)
C(235)	-117(33)	6291(17)	1367(36)	76(18)
C(236)	-86(48)	5989(24)	746(49)	161(38)

Table 18. Atomic co-ordinates for compound 6.(continued)

C(237)	248(29)	6722(15)	1440(31)	62(14)
C(238)	-1095(21)	6286(11)	1350(23)	29(10)
In(3)	5032(3)	6949(1)	2533(3)	33(2)
P(31)	6448(7)	6719(3)	2654(8)	37(3)
C(311)	6938(20)	6365(12)	3632(22)	18(9)
C(312)	6922(27)	6693(15)	4344(29)	66(15)
C(313)	7740(28)	6221(16)	3709(32)	73(16)
C(314)	6406(36)	6028(18)	3823(40)	118(24)
C(315)	6323(27)	6399(14)	1715(27)	27(12)
C(316)	5763(28)	6617(15)	1045(30)	62(15)
C(317)	5827(26)	5975(13)	1649(28)	62(14)
C(318)	7052(25)	6212(14)	1637(28)	57(13)
P(32)	3941(6)	6352(3)	2348(7)	29(2)
C(321)	3716(21)	6455(11)	3308(22)	15(9)
C(322)	4367(42)	6430(23)	3955(49)	158(35)
C(323)	3089(39)	6113(21)	3357(44)	138(29)
C(324)	3253(31)	6915(15)	3319(34)	83(16)
C(325)	3136(28)	6514(15)	1262(30)	45(13)
C(326)	3615(33)	6448(17)	805(35)	80(19)
C(327)	2745(20)	6913(11)	1343(22)	35(9)
C(328)	2463(25)	6161(14)	1233(28)	58(13)
P(33)	4642(9)	7741(4)	2549(9)	48(3)
C(331)	5317(37)	7947(19)	3331(39)	86(21)
C(332)	5268(33)	7691(17)	4117(33)	84(18)
C(333)	5161(29)	8422(15)	3610(31)	74(16)
C(334)	6162(41)	7979(22)	3473(46)	148(31)
C(335)	4801(18)	7977(9)	1509(20)	0(7)
C(336)	4268(31)	7688(16)	852(33)	83(18)
C(337)	5713(30)	7938(17)	1594(35)	94(18)
C(338)	4540(28)	8454(14)	1512(28)	67(15)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Atomic co-ordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2 x10^3$)

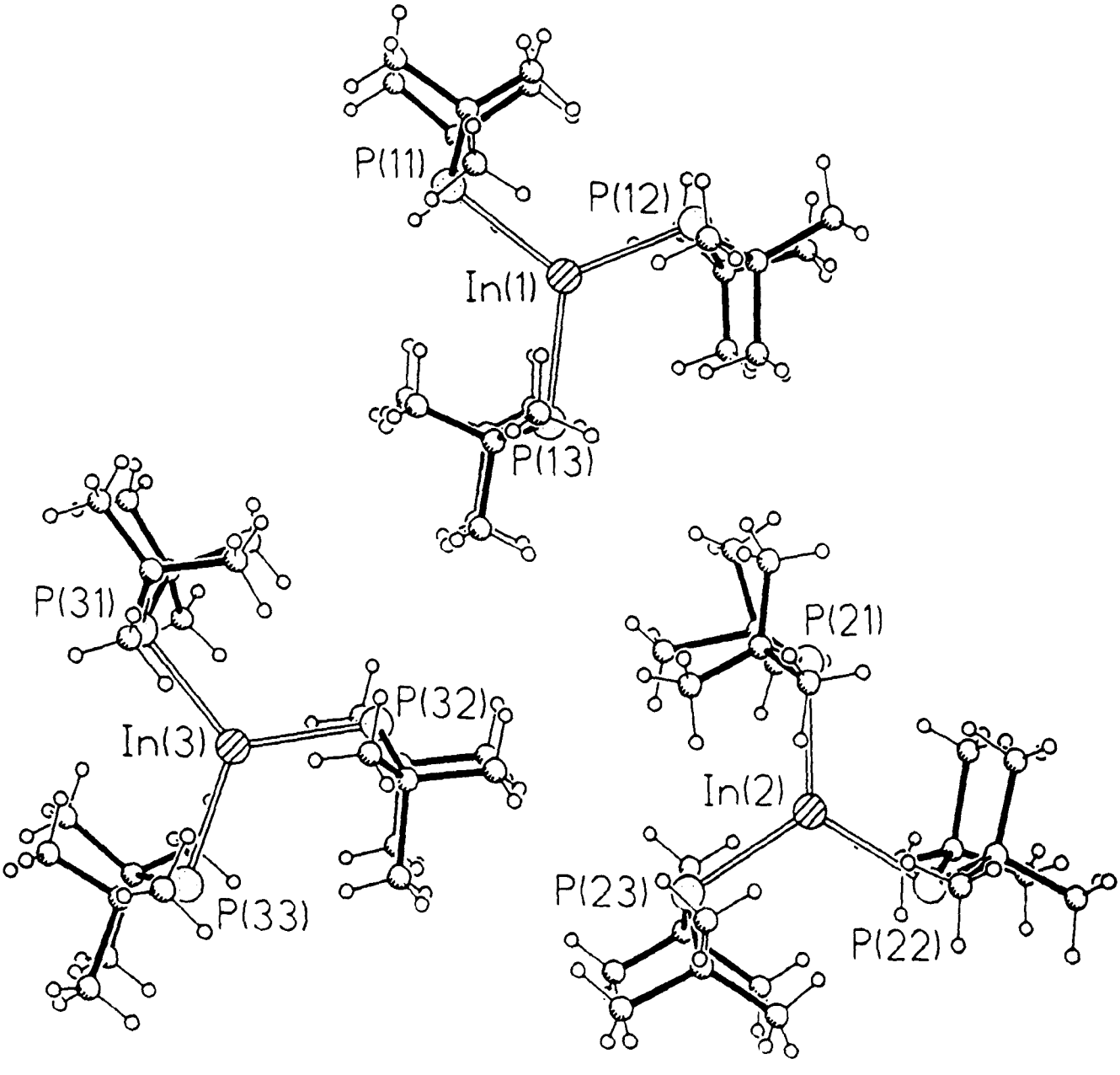


Diagram 1. View of the three different molecules in the unit cell for the structure of compound 6.

Compound 7. $[(Et_2InPBu^t_2)_2]$

For this compound the data were collected and the structure was refined by Dr. M. McPartlin and Dr. H. R. Powell (The Polytechnic of North London). The structure was determined by the heavy atom method. Anisotropic temperature factors were used for all non-hydrogen atoms. The bond lengths and angles are given in Tables 19 and 20. The atomic co-ordinates of the non-hydrogen atoms are given in Table 21.

The ethyl groups in this compound were found to be disordered. This disorder is shown in the view of the unit cell shown in Diagram 2. The molecule was found to be dimeric, the second half of the dimer being symmetry generated.

Table 19. Bond lengths for compound 7, (Å).

In	-P(1)	2.635(2)	In	-C(21)	2.170(13)
In	-C(31)	2.176(12)	P(1)	-C(11)	1.879(8)
C(11)	-C(12)	1.520(12)	C(11)	-C(13)	1.497(13)
C(11)	-C(14)	1.520(13)	C(21)	-C(22)	1.503(1)
C(31)	-C(32)	1.597(1)			

Table 20. Bond angles for compound 7, (°).

C(21)	-In	-P(1)	114.1(2)	C(31)	-In	-P(1)	113.3(3)
C(31)	-In	-C(21)	113.5(5)	In	-P(1)	-In'	94.4(1)
C(11)	-P(1)	-In	112.2(3)	P(1)	-In	-P(1')	85.6(1)
C(12)	-C(11)	-P(1)	107.6(6)	C(13)	-C(11)	-P(1)	113.2(7)
C(13)	-C(11)	-C(12)	106.4(8)	C(14)	-C(11)	-P(1)	112.3(7)
C(14)	-C(11)	-C(12)	107.7(8)	C(14)	-C(11)	-C(13)	109.2(9)
C(11)	-P(1)	-C(11')	112.7(6)	C(22)	-C(21)	-In	116.0(3)
C(32)	-C(31)	-In	117.0(3)				

Table 21. Atomic co-ordinates for compound 7.

Atom	x	y	z	U_{iso} or U_{eq}
In	0.11585(10)	0.00000	0.40686(19)	0.0610(10)
P(1)	0.0000	0.1543(5)	0.5000	0.058(3)
C(11)	0.0478(11)	0.2440(15)	0.6566(21)	0.078(10)
C(12)	0.0844(13)	0.1622(17)	0.7752(20)	0.092(11)
C(13)	0.1251(15)	0.3179(23)	0.6119(27)	0.131(13)
C(14)	-0.0231(16)	0.3192(21)	0.7274(28)	0.131(13)
C(21)	0.2435(16)	0.0000	0.5290(31)	0.111(14)
C(22)	0.3188(16)	-0.0653	0.4590(31)	0.117(16)
C(31)	0.1300(20)	0.0000	0.1669(29)	0.130(14)
C(32)	0.2134(20)	0.0692	0.1026(29)	0.137(16)

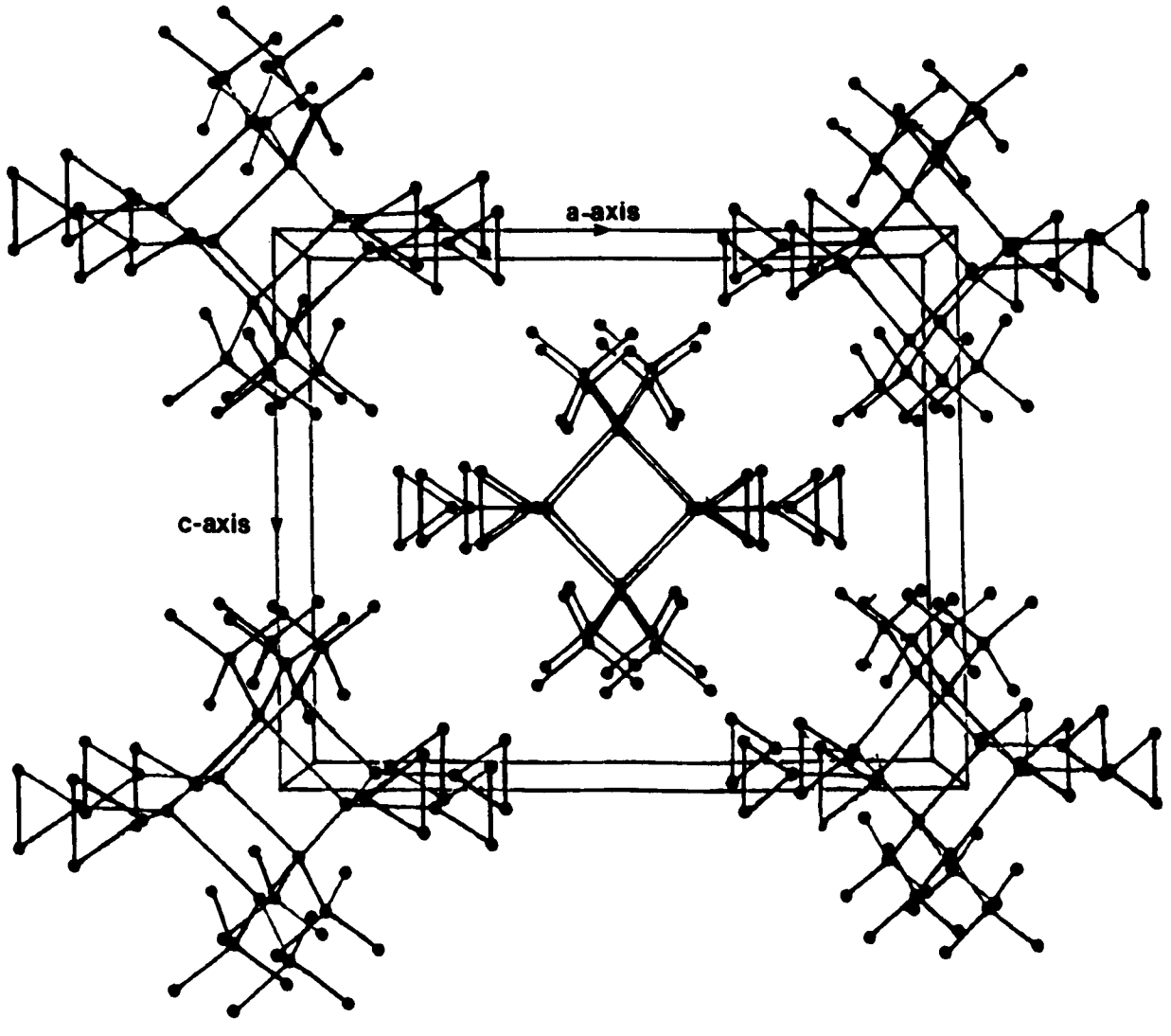
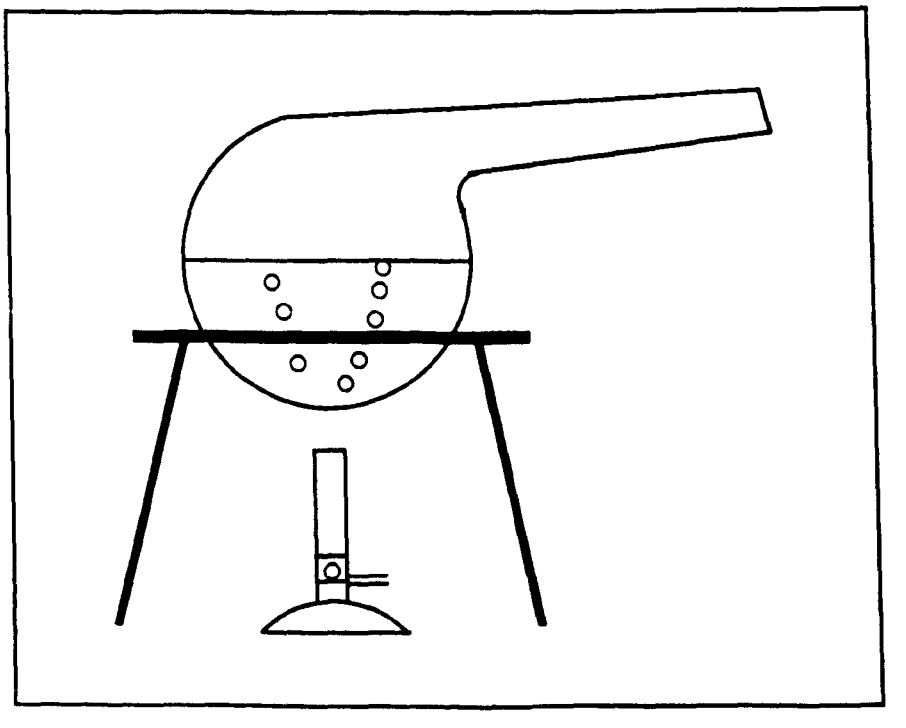


Diagram 2. View of the unit cell of compound 7 showing the disorder in the ethyl groups.

APPENDIX C

EXPERIMENTAL



General Experimental.

Except where otherwise stated all of the compounds were air or moisture sensitive and were, therefore, handled either in a nitrogen or argon filled glove box or under nitrogen on a Schlenk line using standard techniques. All solvents were dried prior to use and distilled under nitrogen. Tetrahydrofuran, diethylether, toluene, benzene and hexane were all freshly distilled from sodium/benzophenone. Dichloromethane and acetonitrile were freshly distilled from calcium hydride. N.m.r. solvents were dried over 3 Å molecular sieve (supplied by Sigma) prior to use.

^{1}H-N.m.r. spectra were run on a Perkin Elmer R34 (220 MHz) spectrometer and chemical shifts are quoted relative to TMS. Infra-red spectra were run on a Perkin Elmer 580B Spectrophotometer. ^{31}P- and ^{115}In-n.m.r.spectra were obtained on a Bruker W.H. 400 MHz spectrometer at 161.92 and 87.61 MHz respectively. The ^{31}P-N.m.r. chemical shifts are qouted relative to an external standard (H_3PO_4). The 115In-n.m.r. spectra are quoted relative to an external standard of 0.5 mol dm-3 $[In(H_2O)_6]^{3+}$ in D_2O. The Raman spectra were run by Dr. J. D. Woollins of Imperial College, London.

Indium analyses were carried out on dilute nitric acid solutions (*ca* 1 mol dm^{-3}) of the compounds on a Varian Techtron AA6 atomic absorption spectrometer. The wavelength used in these analyses was The spectrometer was calibrated each time of use on standard solutions of indium of concentrations in the range 20-100 $\mu g\ ml^{-1}$. These standard solutions were prepared by dissolving a known weight of indium metal in concentrated nitric acid followed by dilution to a known volume in a volumetric flask. A calibration curve was then plotted of concentration

against absorption. This plot is slightly curved, however, for the range of concentrations of unknown samples used (typically 30-60 $\mu g\ ml^{-1}$) it is reasonable to approximate this to a straight line.

Carbon, hydrogen, nitrogen and iodide analyses were carried out by Butterworths or Medac. For this, small samples were sealed in glass tubes under vacuum, to prevent deterioration of the compounds while in transit.

Dicyclohexylphosphine and 1,2-bis(diphenyl-phosphino)ethane were supplied by Strem Chemicals, Danvers, Massachusetts. Triisobutylphosphine was supplied by Maybridge Chemical Co., Tintagel, Cornwall. Trimethylphosphine was prepared according to the method of Green *et al.*[153] All of the liquid phosphines were dried over 3 Å molecular sieves prior to use. Indium metal was supplied by Johnson Matthey and was 99.999% pure.

Preparation of Di-*t*-butylphosphine. Di-*t*-butylphosphine was prepared according to the method of Hoffmann and Schellenbeck.[154] A typical preparation is given. A solution of 2-chloro-2-methylpropane (500 g; 5.40 mol) in diethylether (500 ml) was added dropwise to a stirred mixture of magnesium (125 g; 5.14 mol) and diethylether (300 ml) with cooling in an ice bath. After completion of the reaction the yield of Grignard reagent was determined by removing a 10 cm^3 aliquot and hydrolysing this with a known amount of dilute hydrochloric acid. The Grignard was then determined by a back titration with standardised sodium hydroxide solution and phenolphthalein indicator. Typical yields were of the order of 70%. Assuming this then, phosphorus trichloride (241 g; 1.76 mol) dissolved in diethylether (1500 cm^3) was added dropwise to the Grignard solution (3.60 mol) which was stirred throughout with a powerful overhead stirrer (it is essential to ensure good stirring during

this addition as the formation of a thick white precipitate occurs during the reaction which may become so thick as to prevent the stirrer operating). Towards the end of the reaction diethylether (1000 cm^3) was added to help dilute the slurry that formed. After completion of this stage of the reaction, the mixture was filtered through *ca.* 3 cm depth of dried celite on top of a large sinter. A water pump was used to help draw the solution through the large quantity of magnesium chloride (formed during the reaction) that settles on top of the celite. The diethylether was then removed by distillation to leave crude di-*t*-butylphosphoruschloride. Typical yield 70 g (22%). The help of Mr H. G. Beaton and Mr. G. A. Pike in this preparation is gratefully acknowledged. The Bu^t_2PCl was identified from its $^{31}P\{^1H\}$-n.m.r.spectrum, δ147 ppm. Occasionally, if the reaction mixture was not stirred efficiently or if the Grignard reagent was incorrectly determined a quantity of Bu^tPCl_2 was also produced, δ199 ppm.

The Bu^t_2PCl was converted into the phosphine by reduction with $LiAlH_4$. A typical procedure for this is given. Crude di-*t*-butylphosphoruschloride (70 g; 0.39 mol) in diethylether (100 cm^3) was added slowly to a stirred suspension of $LiAlH_4$ (20 g; 0.53 mol) in diethylether (100 cm^3). After addition, the $LiAlH_4$ was destroyed (cautiously) with water (5 cm^3), sodium hydroxide solution (1.0 mol dm^{-3} ; 10 cm^3) and then water was added dropwise until the solid in the reaction mixture was completely white. The reaction mixture was extracted with diethylether (100 cm^3 x 5). The diethylether extractions were combined and the the diethylether removed by distillation. The di-*t*-butylphosphine residue was purified twice by fractional distillation. (distilling at 65°C at a pressure of *ca.* 25 mm Hg). Typical yield, 40 g (70 %). The Bu^t_2PH was identified from its $^{31}P\{^1H\}$-n.m.r.spectrum, δ19 ppm.

Preparation of Indium Triiodide. Indium triiodide was prepared by a modification of a literature method.[155] A typical method is given. Indium metal (foil) (5 g; 43.6 mmol) was added to a solution of iodine (16.4 g; 64.6 mmol, I_2) in diethylether (50 cm^3). The mixture was cooled in ice and stirred until all of the purple/brown iodine colouration had dissipated. The solution was filtered to remove any remaining indium metal and the diethylether was removed under reduced pressure with heating to 100°C to remove the final traces. The resulting yellow powder was washed with hot toluene (30 cm^3) which was allowed to cool to room temperature before the product was isolated by filtration. The bright yellow powder thus obtained was dried *in vacuo* for three hours. Typical yield, 19 g (90%). (Analysis,found: In, 22.8%. InI_3 requires In, 23.2%).

Preparation of Indium Trichloride. Indium metal (150 g; 1.31 mol; beaten into foil) was reacted with 500 cm^3 of concentrated hydrochloric acid (this took five days to dissolve). After the last of the indium had reacted the solution was boiled to dryness. This gave a hygroscopic white solid (305 g). This was placed in a quartz tube and dried *in vacuo* at 200 °C. This gave a quantitative yield of crude $InCl_3$. This was stored under nitrogen and sublimed in small quantities as required. The sublimation was carried out at *ca.* 300 °C under a vacuum of 10^{-3} mm Hg. The sublimation of *ca.* 10 g of this crude $InCl_3$ typically resulted in a yield of *ca.* 7 g of pure crystalline $InCl_3$. The remaining 3 g of material presumably was indium oxide or indium hydroxide. Typical analysis, found In, 51.1%. $InCl_3$ requires 51.9%.

Preparation of $InCl_3(PMe_3)_2$. Indium trichloride (1.68 g; 7.59 mmol) was dissolved in THF (20 cm^3) and trimethylphosphine (1.16 g; 15.3 mmol) was added from a syringe at room temperature. The solution was concentrated under reduced pressure (to *ca.* 5 cm^3) and hexane (10 cm^3) was added. This produced a microcrystalline, colourless solid that was recrystallised from a THF/hexane mixture.
Yield, 2.37 g (83%). Crystals of this compound suitable for the *X*-ray diffraction study were grown from a THF solution layered with hexane (1:4) at room temperature.

The 1:1 phosphine complexes of indium triiodide were all prepared by the same method. The method used for the preparation of the di-*t*-butylphosphine complex is given as a standard preparative method.

Preparation of $I_3In.HPBu^t_2$.

To a solution of indium triiodide (2.85 g, 5.75 mmol) in diethyl ether (50 cm^3) at room temperature was added a solution of di-*t*-butylphosphine (0.84 g, 5.76 mmol) in diethyl ether (10 cm^3). A colourless crystalline product immediately precipitated. This was separated by filtration under nitrogen and recrystallised from hot toluene. The colourless crystalline product obtained was isolated by filtration and dried *in vacuo*. Yield, 3.35 g (91%). (Analysis,found: C, 14.91; H, 3.12; In, 17.2%. $C_8H_{19}PInI_3$ requires C, 14.96; H, 2.96; In, 17.9%). N.m.r. ($CDCl_3$): δ_H 1.64 (18 H, d, CH_3), 3.98 and 5.57 (1 H, d, PH).

Crystals of this complex suitable for the *X*-ray diffraction study were grown from hexane solution at -5 °C.

Preparation of $I_3In.PBu^i_3$. This adduct was prepared by the above procedure. Triisobutylphosphine (2.37 g; 11.7 mmol) was added to indium triiodide (5.81 g, 11.7 mmol) in diethylether (30 cm^3). The product was a colourless crystalline solid. Yield, 6.21 g (76%). (Analysis,found: C, 20.66; H, 3.94; I, 54.35; In, 16.2%. $C_{12}H_{27}PInI_3$ requires C, 20.65; H, 3.90; I, 54.55; In, 16.5%). N.m.r. ($CDCl_3$): δ_H 0.84 (6 H, d, CH_3), 1.53 (2 H, m, CH_2), and1.93 (1 H, m, CH).

Preparation of $I_3In.HPCy_2$. This adduct was prepared by the above procedure. Dicyclohexylphosphine (1.13 g; 5.71 mmol) was added to indium triiodide (2.83 g, 5.72 mmol) in diethylether (20 cm^3). The product was a colourless crystalline solid. Yield, 3.64 g (91%).(Analysis,found: C, 21.30; H, 3.50; In, 16.0%. $C_{12}H_{23}PInI_3$ requires C, 20.76; H, 3.32; In, 16.6%). N.m.r. ($CDCl_3$): δ_H 1.37, 1.90, 2.56 (22 H, m, C_6H_{11}), 3.74 and 5.36 (1 H, d, PH).

Preparation of $I_3In.HPPh_2$. This adduct was prepared by the above procedure. Diphenylphosphine (1.81 g; 9.73 mmol) was added to indium triiodide (4.82 g, 9.73 mmol) in diethylether (30 cm^3). The product was a colourless crystalline solid. Yield, 4.91 g (72%).(Analysis,found: C, 20.96; H, 1.66; In, 17.2%. $C_{12}H_{11}PInI_3$ requires C, 21.12; H, 1.61; In, 16.8%). N.m.r. ($CDCl_3$): δ_H 5.76 and 7.48 (1 H, d, PH), and 7.7 (10 H, m, C_6H_5).

Crystals of this complex suitable for the *X*-ray diffraction study were grown from hexane solution at -5 °C.

The melting points and infra-red data for the above complexes are given in Table 1.

Table 1. Infra-red data and melting points (°C) for the $I_3In.PR_3$ complexes.

Complex(M.Pt.)	Infra-red bands. (Nujol mull, CsI plates)
$I_3In.PBu^t_3$ (176-179 °C)	820(m),848(m),972(m,br),1074(m),1100(m),1165(m) 1250(m),1307(w),1345(W),1402(w).
$I_3In.HPBu^t_2$ (126-132 °C)	468(m),767(vs),813(w),867(w),945(m),1028(s), 1179(s),1211(w),1310(w),1410(w),2364(vw).
$I_3In.HPCy_2$ (127-129 °C)	285(w),307(w),364(w),379(w),439(m),463(m),511(m), 699(w),739(m),782(s),793(s),826(w),851(m),870(m), 892(m),910(m),922(m),939(m),1003(s),1009(s), 1031(m),1047(m),1080(m),1086(m),1116(s),1124(s), 1178(s),1184(s),1200(s),1208(s),1270(s),1300(s), 1330(m),1347(m),1360(m),1447(s),2355(vw).
$I_3In.HPPh_2$ (214-218 °C)	345(w),402(w),430(m),457(m),507(s),691(s),740(s), 748(s),787(s),875(m),918(w),999(w),1026(w),1069(w), 1100(m),1108(m),1159(w),1184(w),1307(w),1332(m), 1438(s),1573(m),3060(w).

Preparation of InI_3(Diphos). To a solution of indium triiodide (1.76 g; 3.35 mmol) in acetonitrile (10 cm^3) was added a solution of diphos (1.41 g; 3.55 mmol) in acetonitrile (20 cm^3) at room temperature. After concentrating under reduced pressure to approximately half the original volume, hexane (10 cm^3) was added. This caused the precipitation of a colourless solid that was isolated by filtration under nitrogen and dried *in vacuo*. Yield, 2.32 g (73%).(Analysis,found: C, 34.75; H, 2.80%. $C_{29}H_{24}P_2InI_3$ requires C, 34.93; H, 2.71%). N.m.r. ($CDCl_3$): δ_H 2.55 (4 H, s, CH_2) and 7.51 (20 H, m, C_6H_5). $^{31}P\{^1H\}$-n.m.r. ($C_6D_5CD_3$): δ -19 ppm.

Preparation of $InI_3(Diphos)_2$. This addduct was prepared by the above method. Indium triiodide (1.36 g; 2.75 mmol) was reacted with diphos (2.19 g; 5.51 mmol) in acetonitrile (40 cm^3). The product was a colourless solid. Yield, 2.79 g (78%).(Analysis,found: C, 47.57; H, 3.80%. $C_{58}H_{48}P_4InI_3$ requires C, 48.33; H, 3.72%). N.m.r. ($CDCl_3$): δ_H 2.33 (4 H, s, CH_2) and 7.42 (20 H, m, C_6H_5), $^{31}P\{^1H\}$-n.m.r. ($C_6D_5CD_3$): δ -16 ppm.

The infra-red data for the above two complexes is given in Chapter 2, Table 5 (page 87).

Crystals of $(InI_3)_2(Diphos)_3$ were grown by layering an acetonitrile solution of $InI_3(Diphos)$ with hexane (1:4) at -5 °C. The crystals used were found on the sides of the vessel in the hexane layer.

Experimental (Chapter 3).

The preparation of $I_3In.HPBu^t_2$ has been described already. $I_3In.PPh_3$ was prepared according to the method previously used by Carty and Tuck,[20] except that the product was recrystallised from hexane.

Preparation of $MeInI_2.PPh_3$. A solution of $I_3In.PPh_3$ (0.84 g; 1.11 mmol) in toluene (20 cm^3) was added slowly to a methyllithium solution in diethylether (0.67 cm^3; 1.11 mmol). The solution turned slightly cloudy on addition and was left stirring for 12 hours. After this time the solution was filtered and concentrated under reduced pressure to a volume of *ca.* 2 cm^3. This was mixed with 10 cm^3 of hexane and cooled to -20 °C overnight. This gave a colourless microcrystalline powder that was isolated by filtration and dried *in vacuo*. Yield, 0.56 g (78 %). Analysis, found: C, 35.60; H, 2.96; I, 38.89; In, 17.2%. $C_{19}H_{18}PInI_2$ requires

C, 35.33; H, 2.81; I, 39.31; In, 17.8%. N.m.r. ($CDCl_3$): δ_H 0.71 (3 H, s, CH_3), and 7.57 (15 H, m, C_6H_5). $^{31}P\{^1H\}$-N.m.r. ($CDCl_3$): δ -16.1 ppm.

Preparation of $Me_2InI.PPh_3$. This adduct was prepared by the above method. $InI_3.PPh_3$ (1.13 g; 1.49 mmol) was reacted with methyllithium in diethylether (1.80 cm^3; 2.98 mmol). The product was a colourless solid. Yield, 0.66 g (83 %). Analysis, found: C, 44.44; H, 4.01; I, 24.27; In, 20.9%. $C_{20}H_{21}PInI$ requires C, 44.97; H, 3.93; I, 23.78; In, 21.5%. N.m.r. ($CDCl_3$): δ_H 0.36 (6 H, s, CH_3), and 7.52 (15 H, m, C_6H_5). $^{31}P\{^1H\}$-N.m.r. ($CDCl_3$): δ -11.4 ppm.

Preparation of $Me_3In.PPh_3$. This compound was prepared by the above method. $InI_3.PPh_3$ (1.62 g; 2.14 mmol) was reacted with methyllithium in diethylether (3.9 cm^3; 6.4 mmol). The product was a colourless solid. Yield, 0.62 g (69 %). N.m.r. ($C_6D_5CD_3$): δ_H 0.07 (9 H, s, CH_3), 7.43 and 7.06 (15 H, m, C_6H_5). $^{31}P\{^1H\}$-N.m.r. ($CDCl_3$):(C_6D_6): δ -6.3 ppm.

Preparation of $MeInI_2.HPBu^t_2$. This compound was prepared by the above method. $InI_3.HPBu^t_2$ (0.49 g; 0.76 mmol) was reacted with methyllithium in diethylether (0.46 cm^3; 0.76 mmol). The product was a colourless solid. Yield, 0.34 g (84%). Analysis, found: C, 21.06; H, 4.62; I, 47.01; In, 20.8%. $C_9H_{22}PInI_2$ requires C, 20.43; H, 4.16; I, 47.92; In, 21.7%. N.m.r. ($CDCl_3$): δ_H 0.79 (3 H, s, CH_3), 1.07 (18 H, d, C_4H_9), 3.76 and 5.27 (1 H, d, PH). $^{31}P\{^1H\}$-N.m.r. ($CDCl_3$): δ 11.9 ppm.

Preparation of $Me_2InI.HPBu^t_2$. This compound was prepared by the above method. $InI_3.HPBu^t_2$ (0.72 g; 1.12 mmol) was reacted with methyllithium in diethylether (1.36 cm^3; 2.24 mmol). The product was a colourless solid. Yield, 0.31 g (66%). Analysis, found: C, 28.18; H, 6.30; I, 31.43; In,27.1%. $C_{10}H_{25}PInI$ requires C, 28.73; H, 6.03; I, 30.38; In, 27.5%. N.m.r. ($C_6D_5CD_3$): δ_H 0.44 (6 H, s, CH_3), 1.07 (18 H, d, C_4H_9), 3.76 and 5.27 (1 H, d, PH). $^{31}P\{^1H\}$-N.m.r. ($CDCl_3$): δ 14.4 ppm.

Preparation of $(Me_2InPBu^t_2)_2$. To a solution of $InI_3.HPBu^t_2$ (1.17 g; 1.82 mmol) in toluene (20 cm^3) was added a diethylether solution of methyllithium (3.31 cm^3; 5.46 mmol). This caused an immediate white precipitate. After stirring for 12 hours the solution was filtered and then heated to 60 °C for 1 hour. After this time the solution was allowed to cool and then concentrated under reduced pressure to *ca.* 2 cm^3, mixed with hexane (10 cm^3) and cooled to -20 °C for 12 hours. This resulted in a colourless crystalline product which was isolated by filtration and dried *in vacuo*. Yield, 0.31 g (58 %). Analysis, found: C, 41.40; H, 8.28; In, 38.5%. $C_{10}H_{24}PIn$ requires C, 41.40; H, 8.25; In, 39.6%. N.m.r. ($C_6D_5CD_3$): δ_H 0.24 (6 H, s, CH_3), and 1.32 (18 H, d, C_4H_9). $^{31}P\{^1H\}$-N.m.r. (C_6D_6): δ 39.2 ppm.

The infra-red spectra of the above compounds are summarised in Table 2.

Table 2. Infra-red Data of the methyl derivatives of $InI_3.PR_3$ (Bu^t_2PH and PPh_3).

Compound	Infra-red Bands (cm^{-1}).
$MeInI_2PPh_3$	439(w),495(s),503(m sh),520(s),691(s),711(m), 746(s),1000(m),1027(w),1099(s),1154(w),1181(w), 1309(w),1379(w),1438(s).
$Me_2InI.PPh_3$	397(w),436(m),488(m),496(s),517(s),692(s),709(s), 745(s),844(w),998(m),1028(m),1070(w),1097(s), 1155(m),1161(m),1180(m),1307(m),1328(m),1436(s).
$MeInI_2.HPBu^t_2$	406(w),465(w),502(m),773(s),816(m),871(m),944(m), 1026(s),1175(s br),1208(w).
$Me_2InI.HPBu^t_2$	406(w),466(w),481(s),505(s),702(s br),771(s),817(m), 880(m),942(w),1026(s),1147(w),1176(m),1262(w), 1370(s),2427(m).
$(Me_2InPBu^t_2)_2$	476(s),503(w),535(w),603(w),652(m),689(s),819(m), 936(m),1011(m),1021(m),1056(w),1147(m), 1172(m br),1206(w),1369(s).

Preparation of $LiPBu^t_2$. To a solution of di-*t*-butyl phosphine (5.8 g; 39 mmol) in hexane (50 cm^3) was added dropwise a hexane solution of *n*-butyllithium (16.5 cm^3; 39 mmol). The solution was heated to 60 °C for two hours. While being heated a white precipitate formed. The solution was cooled to -5 °C for 1 hour and then the white precipitate was separated by filtration and dried *in vacuo* . Yield, 5.1 g (85 %) . (Contrary to a previous report [156] this compound was found to be pure white and not yellow. Contamination of the product with traces of diethyl ether or tetrahydrofuran produced a bright yellow colour change).

Preparation of $In(PBu^t_2)_3$. A suspension of $LiPBu^t_2$ (2.31 g; 15.2 mmol) in toluene (20 cm^3) was added slowly to a suspension of indium triiodide (2.50 g; 5.0 mmol) in toluene (20 cm^3) with cooling to -78 °C.

The resulting mixture was stirred for 30 minutes and then allowed to warm to room temperature. After a further hour the reaction mixture had the appearance of a deep red solution and a fine, pale precipitate. The solution was filtered through a fine porosity sinter under argon and concentrated under reduced pressure to *ca.* 4 cm^3. To this was added 100-120° fraction petroleum ether and the resulting solution was cooled to -78 °C for 2 hours. This gave a small crop of bright red crystals which were isolated by filtration and dried *in vacuo*. Yield, 0.61 g (22 %). Analysis, found: C, 52.15; H, 10.17%. $C_{24}H_{54}P_3In$ requires C, 52.38; H, 9.82%. Melting point, 170-174 °C. $^{31}P\{^1H\}$-nmr, δ (C_6D_6): 71.8 ppm, singlet . ^1H-nmr, δ_H ($C_6D_5CD_3$): 1.49 (d, CH_3) J_{PH} = 11.1 Hz.

Experimental (Chapter 4).

Trimethylindium was prepared from methyllithium and indium trichloride according to the method of Clark and Pickard.[59] Trimethylindium was obtained as an ether solution after distillation (*ca.* 110°C at 25 mmHg). Its concentration was determined using a titration with EDTA and zinc acetate solutions on a hydrolysed sample, according to the method described by Coates and Graham.[157] The solution was found to contain 53.8 % (w/w) of trimethylindium.

Triethylindium was prepared according to the method of Todt and Dötzer [138] from indium metal, magnesium and bromoethane in diethyl ether. It was obtained free of ether by fractional distillation from a mixture with benzene (*ca.* 65 °C at 1 mmHg).

The infra-red data for the following compounds is given in Table 11, Chapter 4 (page 156).

Preparation of Dimethyl(salicylaldehyde)indium.

Salicylaldehyde (0.61 g; 5.00 mmol) was added slowly to a stirred solution of trimethylindium (4.99 mmol) in hexane (20 cm^3) at room temperature. A yellow powder was immediately precipitated. This was separated by filtration and recrystallised from a mixture of dichloromethane and hexane to give a yellow crystalline product. Yield, 0.84 g (64%). Analysis, found: C, 40.46; H, 4.03; In, 44.4%. $C_9H_{11}O_2In$ requires C, 40.64; H, 4.17; In, 43.2% N.m.r. ($CDCl_3$): δ_H -0.02 (6 H, s, CH_3), 6.91 (2 H, m, C_6H_4), 7.48 (2 H, m, C_6H_4), and 9.44 (1 H, s, CHO).

Crystals of this compound suitable for X-ray diffraction were grown from a chloroform solution of the compound layered with hexane (1:4).

Preparation of Dimethyl(2-carboxybenzaldehyde)indium.

2-Carboxybenzaldehyde (0.58 g; 3.86 mmol) was added slowly to a stirred solution of trimethylindium (3.87 mmol) in hexane (20 cm^3) at room temperature. The reaction mixture was heated to 50°C for 30 minutes to ensure completion and allowed to cool. Removal of the solvent under reduced pressure left a white solid which was recrystallised from a tetrahydrofuran/hexane mixture to give a white microcrystalline product. This was filtered and dried *in vacuo*. Yield, 0.55 g (48%). Analysis,found: C, 40.68; H, 3.79; In, 38.3%. $C_{10}H_{11}O_3In$ requires C, 40.85; H, 3.77; In, 39.1%. N.m.r. [$(CD_3)_2SO$]: δ_H -0.23 (6 H, s, CH_3), 7.43, 7.74, 7.97 (4 H, m, C_6H_4), and 10.39 (1 H, s, CHO).

Preparation of Dimethyl(N,N'-diphenylacetamidine)indium.

N,N'-Diphenylacetamidine (0.82 g, 4.18 mmol) was added slowly to a stirred solution of trimethylindium (4.19 mmol) in toluene (20 cm^3) at room temperature. This immediately gave a pale yellow solution which

was concentrated under reduced pressure to a volume of *ca.* 2 cm^3 and mixed with hexane (10 cm^3) . On cooling to -20 °C for 3 hours a white crystalline product was obtained. This was recrystallised from hexane and dried *in vacuo*. Yield, 0.82 g (58%). Analysis, found: C, 54.03; H, 5.35; N, 7.90; In, 33.1%. $C_{16}H_{19}N_2In$ requires C, 54.26; H, 5.41; N, 7.91; In,32.5%. N.mr. ($C_6D_5CD_3$): δ_H 0.03 (6 H, s, CH_3), 1.58 (3 H, s, CH_3), 6.90 and 7.13 (10 H, m, C_6H_5).

Preparation of Dimethyl(2-pyrrolidinone)indium.

2-Pyrrolidinone (0.44 g; 5.17 mmol) was added to a stirred solution of trimethylindium (5.18 mmol) in toluene (20 cm^3) at room temperature. On addition, bubbles of gas were immediately evolved. The reaction mixture was heated to 50 °C for 30 minutes and then the solution was concentrated in vacuo to a volume of *ca.* 2 cm^3. This was mixed with hexane (10 cm^3) and cooled to -20 °C for 3 hours. The white microcrystalline powder that was formed was isolated by filtration and dried *in vacuo*. Yield, 0.51 g (43%). Analysis, found: C, 30.26; H, 5.21; N, 4.78; In, 49.8%. $C_6H_{12}NOIn$ requires C, 31.46; H, 5.24; N, 6.12; In,50.2%. N.m.r. [$(CD_3)_2SO$]: δ_H -0.62 (6 H, s, CH_3), 1.98 (4 H, m, CH_2), and 3.30 (2 H, t, CH_2).

Preparation of Diethyl(ethanolamino)indium.

Ethanolamine (0.34 g; 5.57 mmol) was added slowly to a stirred solution of triethylindium (1.13 g; 5.56 mmol) in tetrahydrofuran (40 cm^3) at room temperature. After 10 minutes the solvent was removed under reduced pressure to leave a microcrystalline white solid. This was recrystallised from a tetrahydrofuran/hexane mixture and dried *in vacuo*. Yield, 0.96 g (74%). Analysis, found: C, 31.02; H, 6.97; N, 6.01; In,49.1%. $C_6H_{16}NOIn$ requires C, 30.93; H, 6.87; N, 6.01; In,49.3% N.m.r. ($C_6D_5CD_3$): δ_H 0.31 (2 H,

t, NH_2), 0.65 (4 H, q, CH_2), 1.50 (6 H, t, CH_3), 2.22 (2 H, m, CH_2), and 3.54 (2 H, t, CH_2).

Preparation of Diethyl(di-*t*-butylphosphido)indium.

A solution of di-*t*-butyl phosphine (0.93 g; 6.37 mmol) in hexane (10 cm^3) was added dropwise to a stirred solution of triethylindium (1.28 g; 6.34 mmol) in hexane (10 cm^3). After addition the solution was heated to 65 °C for 1 hour and then cooled to -20 °C for 3 hours. After this time a white crystalline product was obtained. This was filtered and dried *in vacuo*. Yield, 1.57 g (78%). Analysis, found: C, 45.31; H, 8.81; In, 36.1% $C_{12}H_{28}PIn$ requires C, 45.31; H, 8.81; In, 36.1%. N.m.r. ($C_6D_5CD_3$): δ_H 1.03 (4 H, q, CH_2), 1.32 (18 H, t, CH_3), and 1.57 (6 H, t, CH_3).

Crystals of this compound suitable for *X*-ray diffraction were grown at room temperature from a solution of the compound in hexane.

Preparation of Diethyl(phenylethynyl)indium-triphenylphosphine Adduct.

A solution of phenylethyne (2.50 g; 24.51 mmol) in hexane (10 cm^3) was added slowly to a solution of triethylindium (5.17 g; 25.6 mmol) in hexane (20 cm^3). After addition, the mixture was heated to 50 °C for 30 minutes and then allowed to cool. To this was added a solution of triphenylphosphine (6.40 g; 24.4 mmol) in toluene (50 cm^3). After stirring for 10 minutes the solution was cooled to -20 °C for 8 hours. This gave a white crystalline product which was filtered and recrystallised from hexane. The product was dried *in vacuo*. Yield, 11.63g (89%). Analysis, found: C, 67.19; H, 5.60; In, 21.9%. $C_{30}H_{30}PIn$ requires C, 67.20; H, 5.60; In, 21.4%. N.m.r. ($C_6D_5CD_3$): δ_H 1.08 (4 H, q, CH2), 1.64 (6 H, t, CH_3), 7.0 and 7.3 (20 H, m, C_6H_5).

Reaction of Triethylindium with TEMPO. (Tetramethyl-1-piperidinyloxy, free radical.)

A solution of TEMPO (0.90 g; 5.76 mmol) in hexane (10 cm^3) was added dropwise to a solution of triethylindium (1.16 g; 5.75 mmol) in hexane (10 cm^3) which was cooled to -78 °C. This immediately gave a deep red coloured solution. On warming slowly to room temperature this red colour dissipated, leaving a colourless solution. This solution was concentrated under reduced pressure to *ca.* 10 cm^3 and stored at -20 °C overnight. This gave a crop of colourless crystals that were isolated by filtration and dried *in vacuo*. The product slowly decomposed to a grey powder. Yield, 1.28 g (68%). Analysis, found: C, 47.03; H, 8.89; N, 4.21%. $C_{13}H_{28}NOIn$ requires C, 47.43; H, 8.57; N, 4.26 %. N.m.r. ($C_6D_5CD_3$): δ_H 1.26 (12 H, s, CH_3), 1.60 (6 H, t, CH_3), and 0.8-1.5 (m, CH_2).

Thermal decomposition of $(Et_2InPBu^t_2)_2$: A sample of $(Et_2InPBu^t_2)_2$ (1.07 g, 3.37 mmol) was placed in a quartz tube under an atmosphere of nitrogen and fitted inside a tube-furnace. To the quartz tube was connected a water condenser with a glass T-piece fitted to the other end. To one of the arms of this glass T-piece was attached an inflatable plastic bag (in order to maintain this sealed system at atmospheric pressure during the heating). To the other arm was fitted a rubber septum.

The sample in the quartz tube was heated over a period of three hours up to a final temperature of 700 °C. After every 100 °C rise in temperature a $1cm^3$ sample of the gas inside the apparatus was removed through the rubber septum with a gas tight syringe. This gas sample was injected into a Poropak Q G.C. column. After injection this column was heated from 60 °C to 140 °C over a period of three minutes. The gases separated by this column were identified by E.I. mass spectrometry.

After the heating was complete, there remained in the quartz tube a black solid. There was also a small amount of air-sensitive liquid at the base of the condenser. For the black solid, analysis showed, P, 7.46, C, 1.07%.

APPENDIX D

MASS SPECTRA

The mass spectra reported in this work were carried out by Mr. I. Katyal (University of Warwick) on a Kratos MS80 instrument. The samples were sealed in thin walled glass capillaries prior to the specra being obtained and were introduced into the source by breaking the capillaries open in the air. As this procedure only takes a few seconds we found that no significant deterioration of the samples occurred. (Presumably the time taken for the air to diffuse into the capillary is longer than the exposure time.) The E.I. mass spectra were obtained at 70 electron volts.

E.I. Mass Spectrum of $[(Et_2InPBu^t_2)_2]$.

Measured Mass	% Tot. Ionisation
639	2
629	0
624	4
623	1.7
621	2
609	1
607	1
565	0
524	0
508	1
507	5
495	0
492	1
491	6
489	0
488	1
481	1
479	0
467	0
449	1
437	0
430	2
429	7
428	1.6
419	1
415	0
413	1
412	2
411	4
410	2
406	1
405	2
392	2
391	8
389	1
378	1
377	3
375	1
368	1
367	1
363	1
361	1
342	0
341	2
337	1
329	1
324	0
323	1
310	0
309	2
307	1

Measured Mass	% Tot. Ionisation
297	0
297	0
296	1
295	9
293	2
289	1
287	1
281	0
279	2
276	0
275	0
273	1
267	0
267	0
265	0
262	0
261	2
260	1
259	1
255	0
254	0
251	1
234	0
232	0
231	1
220	1
220	0
219	1
218	1
217	1
206	1
206	0
205	2
204	1
203	1
193	1
192	1
191	1
191	0
190	2
189	1
189	0
180	6
179	1
178	2
177	1
176	5
174	1
173	2
168	1
167	1
166	2
165	2
164	1.1
163	10.8

Measured Mass	% Tot. Ionisation
162	1.1
161	1
159	3
155	0
154	1
154	0
153	2
152	1.4
151	4
150	4
149	6
148	1.4
147	14.8
146	1.3
145	3
142	1
140	3
139	1
138	2
137	1.0
136	5
135	8
134	5
133	3
132	4
126	1
125	0
124	2
123	8
122	3
121	3
120	1
119	1
115	1
115	1.0
114	1
113	1
112	3
111	1
110	1
109	4
108	1
107	3
106	5
105	5
104	1
103	1
98	1
97	2
96	1
95	6
94	5
93	3
92	1
91	1.0

Measured Mass	% Tot. Ionisation
90	1
89	2
86	2
85	1
84	2
83	2
82	2
81	1.2
80	0
79	1
77	2
76	1
75	1
74	1
72	1
71	0
70	0
70	0
69	9
68	2
67	1
65	1
64	0
63	1
62	1.1
61	6
60	2
59	1
58	7
57	1.7
57	1
56	1
55	2
54	1
50	1
46	1
45	1
44	5
43	1
42	1
41	8
39	5
35	14.8
33	6
32	3.4
31	1.0
30	1.7

(1)

Measured Mass	% Tot. Ionisation
545	.1
544	.4
535	.1
528	.3
476	.2
461	.1
460	1.2
459	5.7
458	.1
457	.5
445	.2
444	.4
443	2.1
441	.2
429	.1
413	.1
408	1
394	1
392	5
391	1 8
389	2
376	1
375	6
374	1.9
372	2
344	2
316	5
315	3 6
314	1
313	2
299	6
248	5
247	4 6
245	2
232	1
231	1.6
230	6 9
229	1
228	.4
214	.5
200	.5
179	1.1
172	4
171	3.7
163	1
162	3 0
160	1
145	2 3
143	.1
132	.3
120	.1
115	1.3
104	.8
103	9.4
102	.2
101	.1
87	.9
86	10.0
85	.2
84	.1
58	.2
56	.1
35	3.0
32	.1
30	.4
19	.6
18	1
18	14 9
17	3.5

(2)

Measured Mass	% Tot. Ionisation
518	.3
517	1.7
515	.2
487	2
429	4
428	2.4
426	.2
412	.7
411	5.5
410	.2
409	.5
381	1.0
285	.2
284	.6
279	2
269	.7
268	6.4
267	8.7
266	.9
265	1.0
252	.2
251	2.4
237	4
236	2.1
180	5
179	8.1
177	7
163	4
162	7 8
160	6
145	1 0
139	3
132	4
122	3
121	6
114	4 1
112	2
65	2
39	2
35	7 2
32	3
30	2
19	2
19	1.5
18	3
18	13 9
17	7 7

(3)

Measured Mass	% Tot. Ionisation
270	1
268	1
267	4
266	3.7
265	1
264	2
262	2
254	1
253	3
252	2.3
251	10 5
250	4
249	1 2
246	1
238	1
237	1 2
236	9 2
235	2
234	7
223	1
222	4
209	1
208	1 7
207	1
206	1
149	1
146	1
145	5 8
144	2
143	3
136	1
135	1
131	3
130	2.5
129	2
128	2
127	1
126	1
125	1
124	1
123	4
122	3 9
121	4 2
120	2
119	1
118	2
114	12 4
112	2 0
112	1
109	1
107	1

Measured Mass	% Tot. Ionisation
105	1
104	6
97	1
95	1
94	6
93	1 3
92	5
91	1
85	1
83	1
81	2
80	1
79	2
78	1
77	5
76	1 0
75	2
74	3
73	1
71	1
70	1
69	4
69	1
68	1
67	2
66	9
65	3 9
64	1 0
63	1 9
62	8
61	4
60	1
57	2
56	1
55	4
54	1
53	7
52	1
51	7
50	7
49	2
47	1
43	2
42	1
41	2
40	3
39	3 3
38	1 0
37	4
32	2
29	4
28	6
27	2
26	2
18	1

(1) C.I. (Methane) Mass Spectrum of 2-Pyrrolidinone Derivative of $InMe_3$.

(2) C.I.(Ammonia) Mass Spectrum of Salicylaldehyde Derivative of $InMe_3$.

(3) E.I. Mass Spectrum of Salicylaldehyde Derivative of $InMe_3$.

E.I. Mass Spectrum of $[In(PBut_2)_3]$.

Measured Mass	% Tot Ionisation
425	0.0
417	0.0
411	0.1
393	0.0
391	0.1
379	0.1
378	0.0
377	0.1
363	0.0
361	0.1
355	0.1
353	0.0
351	0.0
349	0.0
338	0.0
337	0.2
336	0.1
335	0.2
329	0.0
324	0.1
323	0.8
322	0.1
321	0.1
320	0.0
319	0.1
313	0.0
311	0.0
308	0.0
307	0.3
306	0.8
305	3.3
304	0.1
303	0.3
297	0.1
295	0.0
294	0.0
293	0.3
292	2.8
291	5.3
290	5.3
289	0.2
281	0.2
280	0.0
279	0.2
277	0.0
275	0.1
273	0.2
272	0.0
269	0.0
268	0.1
267	0.6
266	0.1
265	0.6
264	0.0
263	0.1
262	0.0
261	0.2
259	0.0
251	0.1
250	0.2
249	0.7
248	3.1
247	0.5
245	0.0
241	0.1
239	0.0
237	0.0
236	0.3
235	2.4
234	4.5
233	4.3
231	0.0
229	0.0
225	0.1
223	0.1
221	0.0
220	0.0
219	0.2
218	0.1
217	0.4
216	0.1
215	0.2
211	0.1
210	0.0
209	0.3
208	0.0
207	0.1
206	0.0
205	0.1
204	0.2
203	1.1
202	0.4
201	0.1
200	0.0
199	0.0
195	0.0
194	0.1
193	0.2
192	0.3
191	1.8
190	0.3
189	0.6
187	0.1
186	0.0
185	0.1
183	0.0
180	0.1
179	0.7
178	1.7
177	4.6
176	0.2
175	0.1
173	0.0
169	0.0
167	0.0
165	0.1
164	0.1
163	0.6
162	0.1
161	0.6
160	0.2
159	0.3
153	0.1
152	0.0
151	0.1
149	0.1
148	1.5
147	5.4
146	3.8
145	1.2
143	0.0
139	0.0
138	0.0
137	0.1
136	0.1
135	0.8
133	0.1
132	0.0
131	0.3
129	0.0
125	0.1
124	0.0
123	0.1
122	0.9
121	3.6
120	0.1
119	0.1
117	0.0
111	0.1
110	0.0
109	0.1
107	0.1
106	0.1
105	0.1
104	0.1
103	0.2
101	0.0
99	0.0
97	0.1
96	0.0
95	0.1
93	0.1
92	0.1
91	0.9
90	0.6
89	1.2
88	0.1
87	0.6
86	0.0
85	0.1
83	0.3
81	0.1
79	0.3
77	0.1
75	0.4
74	0.1
73	0.2
72	0.0
71	0.2
70	0.0
69	0.2
68	0.0
67	0.1
63	0.1
62	0.1
61	0.5
60	0.0
59	0.2
58	0.8
57	5.2
56	0.3
55	0.5
53	0.1
51	0.0
48	0.0
47	0.1
46	0.1
45	0.3
43	0.3
42	0.2
41	2.7
40	0.1
39	0.8
38	0.0
30	0.0
29	0.0
29	1.6
28	0.1
27	0.4
18	0.2
17	0.1

E.I. Mass Spectrum of Diphenylacetamidine Derivative of $InMe_3$.

Measured Mass	% Tot. Ionisation
694	0
549	0
548	0
535	0
534	1
533	2
483	0
471	1
470	0
469	1
468	0
467	0
410	0
401	.0
381	.0
380	0
370	0
369	1
368	1
367	0
366	.0
366	.1
365	.1
364	1
363	0
363	0
362	0
357	0
356	1
355	9
354	4.6
353	2
352	.3
351	0
350	0
350	0
349	0
348	0
348	1
346	1
345	0
344	0
343	0
342	0
341	4
340	3.9
339	9.0
338	.3
337	1.2
336	0
336	0

Measured Mass	% Tot. Ionisation
335	.1
334	.0
333	0
332	0
332	0
331	.0
330	.0
329	0
328	.1
328	1
327	1
326	.1
325	1.1
324	6.0
323	8.5
322	1.7
321	6
320	1
320	0
318	0
318	0
317	0
315	0
315	0
314	.0
313	.2
312	.1
311	.1
310	.8
309	1
307	.1
297	0
295	.0
293	0
292	0
290	0
284	1
283	.4
281	0
279	0
274	.0
265	.0
264	0
257	.0
254	.0
251	0
249	0
246	0
242	0
232	0
224	0
223	0
222	0
221	1
218	0

Measured Mass	% Tot. Ionisation
212	0
211	2
210	1.4
210	0
209	2.4
208	5
208	0
207	4
206	1
205	0
201	0
195	1
194	3
193	1
192	1
189	0
182	0
181	0
180	0
179	0
178	0
177	0
175	0
170	1
169	3
169	1
168	0
168	3
167	9
166	1
165	0
159	1
157	0
156	4
154	0
153	0
152	0
151	0
150	0
149	1
147	0
146	2
145	6.3
144	2
143	4
142	0
142	0
141	1
140	1
139	1
138	0
137	1
136	0
135	0
134	0

Measured Mass	% Tot. Ionisation
133	1
132	3
131	1
131	1
130	1.6
129	1
128	2
127	1
126	0
126	0
125	0
124	0
124	0
123	1
122	0
122	0
121	0
120	1
119	8
118	6.6
117	3
116	1
116	0
115	9.5
114	0
113	1.1
112	1
111	0
110	0
109	0
108	0
107	0
106	1
105	2
104	2
103	1
102	0
99	0
98	0
97	1
96	0
95	1
94	0
93	4
92	2
91	4
90	1
89	1
88	0
87	0
85	0
84	0
83	0
83	1
82	0

Measured Mass	% Tot. Ionisation
81	2
80	0
80	0
79	1
78	7
77	0
77	6.6
76	3
75	2
74	1
73	0
71	1
70	0
69	3
68	1
67	1
66	1
65	4
64	2
63	3
62	1
61	0
59	0
58	0
57	2
56	1
55	1
54	0
53	0
52	2
51	2.2
50	4
49	0
45	0
44	2
43	1
42	1
41	3
40	1
40	0
39	.4
38	1
37	0
32	2
30	0

C.I. (Ammonia) Mass Spectrum of $Me_2InI.PPh_3$.

Measured Mass	% Tot. Ionisation
670	.1
669	.2
641	.1
632	.1
631	.3
536	.2
521	.1
520	.8
519	3.5
517	.2
499	.2
448	.2
447	.7
446	.7
445	1.7
425	.1
424	.1
419	.1
417	.1
409	.1
408	1.0
407	4.6
406	.1
405	.2
403	.1
391	.1
390	.1
389	3
387	.2
386	.2
379	1
378	6
377	3.0
375	1
371	.2
370	.5
369	1.2
319	.1
291	.1
281	.1
279	.2
278	.2
277	.1
276	.2
274	2.6
273	4
272	.2
266	.1
265	1.3
264	7.7
263	10.8
262	9.5
261	2.9
260	.3
259	.1
258	1
257	4.6
255	2
242	1
202	.3
201	1
200	3
191	1
187	.2
186	3
185	1.8
184	1.3
183	5.6
182	1
181	2
179	.1
170	3
163	.1
162	2.0
160	1
159	1
157	.3
154	.3
153	.2
152	7
146	1
145	4.9
144	1
143	2
141	2
139	.2
133	.3
132	1.9
131	.1
130	1
128	1
126	1
125	.3
115	3.4
113	.1
109	2
108	1.5
107	1.2
102	1
91	1
81	1
78	2
77	3
65	1
57	1
51	1
39	.1
39	6

E.I. Mass Spectrum of 2-Carboxy benzaldehyde Derivative of $InMe_3$.

Measured Mass	% Tot. Ionisation	Measured Mass	% Tot. Ionisation
443	2	119	1
387	.1	115	15.0
308	1	114	2
295	1	113	9
294	1.1	112	7
293	6	111	.1
291	1	109	.1
281	1	106	2
280	8	105	1.4
279	8.2	104	2.5
277	4	97	1
265	3	95	1
257	1	93	.2
253	1	91	.2
252	1.2	85	.1
251	12.8	83	.2
250	.2	82	.1
249	1.3	81	.3
242	1	79	2
237	2	78	2
236	1.8	77	.9
235	7.9	76	1.8
234	2	75	4
233	4	74	5
223	1	73	1
222	1	71	.2
221	2	69	4
220	1.6	65	2
207	2	57	2
192	6	56	1
189	1	55	2
175	2	52	1
159	1.6	51	.3
157	1	50	7
150	1	49	1
149	1.1	44	.3
148	1.2	43	.2
147	.2	43	.1
146	.2	42	.1
145	7.4	41	.2
144	4	39	2
143	4	38	1
137	1	37	1
134	4	32	9
133	1.0	30	1
131	3		
130	1.4		
129	1		
128	1		
121	1		
120	1		

E.I. Mass Spectrum of $MeInI_2.PPh_3$.

Measured Mass	% Tot. Ionisation	Measured Mass	% Tot. Ionisation	Measured Mass	% Tot. Ionisation	Measured Mass	% Tot. Ionisation
647	.1	151	2	96	1	45	.1
496	.1	150	.1	96	.1	45	.1
384	.7	149	.1	95	.3	44	.3
369	1.7	147	.1	94	.1	43	.8
368	.1	146	.1	93	.1	43	.2
367	.1	145	.6	92	.1	42	.2
355	.1	144	.1	91	.1	41	.8
281	.1	142	2	91	.3	40	.1
279	.1	141	.3	89	.2	39	.7
278	.3	140	.1	88	.1	38	.1
277	.6	139	.3	87	.2	37	.1
276	.1	138	.1	86	.1	36	.1
273	.1	137	.1	85	.3	32	.7
268	.1	135	.1	84	.3	31	.1
264	.3	134	.1	83	.3	29	.3
263	2.8	133	.6	83	.3	29	.1
262	9.9	132	.1	82	.2	28	2.4
261	2.3	131	.1	82	.2	27	.4
260	.6	131	.5	81	.8		
259	.1	130	.3	80	.3		
258	.1	129	.3	79	.2		
257	5.0	128	.1	78	.5		
256	.1	128	.3	77	1.1		
255	.2	128	.4	76	.2		
242	4.3	127	1.6	75	.2		
240	.2	126	.1	74	.2		
228	.1	125	.1	73	.6		
213	.1	124	.1	72	.1		
209	.1	123	.1	71	.4		
208	.1	122	.1	70	.2		
207	.5	121	.1	69	.6		
202	.1	120	.1	69	.1		
201	.2	119	.1	68	.1		
199	.1	117	.1	67	.3		
191	.1	116	.1	66	.1		
186	.2	115	4.7	65	.3		
185	1.5	114	.1	64	.1		
184	2.1	113	.2	63	.3		
183	8.4	113	.2	62	.1		
182	.1	112	.2	61	.1		
182	.3	111	.2	60	.3		
181	.5	110	.1	59	.1		
171	.1	109	.7	58	.1		
170	.4	108	5.6	57	.8		
159	.1	107	2.7	57	.5		
158	.1	106	.2	56	.3		
157	.6	105	.1	56	.2		
155	.1	104	.1	55	.9		
154	.5	103	.1	54	.1		
153	.4	102	.2	53	.2		
152	1.3	101	.1	52	.2		
		100	.1	51	1.6		
		99	.1	50	.5		
		98	.3	49	.1		
		97	.4	47	.1		

E.I. Mass Spectrum of $MeInI_2.Bu^t_2PH$.

Measured Mass	% Tot. Ionisation	Measured Mass	% Tot. Ionisation	Measured Mass	% Tot. Ionisation	Measured Mass	% Tot. Ionisation
531	.1	168	.1	110	.3	52	.1
496	1.4	167	.1	109	.3	51	.1
494	.1	166	.1	108	.1	50	.1
446	.1	165	.1	107	.1	48	.1
386	.1	164	.0	106	.1	47	.1
385	.1	163	.1	105	.1	46	.1
384	2.7	161	.0	101	.1	45	.4
382	.1	159	.0	100	.0	44	.1
369	6.3	157	.0	99	.2	44	.5
367	.3	155	.1	98	.4	43	2.2
281	.0	154	.1	97	.9	43	.3
278	.0	153	.1	96	.6	42	.5
274	.0	152	.2	95	.6	41	2.9
272	.1	151	.1	94	.1	40	.1
268	.2	150	.0	93	.2	39	.8
264	.0	149	.1	92	.1	38	.1
258	.2	147	.1	91	.3	38	.1
257	7.6	146	.4	90	.2	37	.0
256	.1	145	.7	89	.1	36	.2
256	.1	143	.1	88	.0	34	.1
255	.1	142	.3	87	.2	32	.5
255	.8	141	.2	86	.1	31	.2
254	.2	140	.1	85	.7	30	.1
252	.1	139	.1	84	.6	30	.1
250	.1	138	.2	83	1.2	29	1.2
243	.1	137	.1	82	.5	29	.1
243	.0	136	.1	81	.8	28	1.5
242	6.2	135	.1	80	.2	27	.6
240	.3	133	.1	79	.3	26	.1
239	.0	132	.0	78	.1	18	.4
237	.1	131	.1	77	.2	17	3.3
236	.2	130	.5	75	.2	17	.1
229	.1	129	.2	74	.1		
228	.0	129	.1	73	.7		
225	.0	128	.1	72	.1		
223	.0	128	.6	71	1.2		
222	.1	127	5.1	70	.6		
213	.1	126	.1	69	1.6		
211	.0	125	.2	69	.0		
209	.1	124	.2	68	.4		
208	.1	124	.0	67	.7		
208	.0	123	.2	66	.1		
207	.2	122	.1	65	.1		
193	.1	121	.1	63	.1		
185	.1	120	.1	62	.1		
183	.1	120	.0	61	.3		
180	.1	119	.1	60	.3		
179	.0	117	.1	59	.2		
177	.0	116	.1	58	.4		
171	.1	115	6.7	57	5.7		
169	.1	114	.1	57	.1		
		113	.6	56	.9		
		112	.2	55	2.4		
		112	.1	54	.4		
		111	.5	53	.3		

E.I. Mass Spectrum of $Me_2InI.Bu^t_2PH$.

Measured Mass	% Tot. Ionisation
563	.1
549	.1
537	.1
529	.4
527	.0
523	.0
499	.1
489	.1
487	.3
485	.1
471	.1
469	.1
468	.1
467	.4
465	.1
451	.1
437	.2
435	.1
427	.1
419	.0
417	.2
415	.0
407	.1
401	.0
387	.6
385	.1
384	.4
371	.0
369	.8
367	.1
357	.4
341	.1
329	.0
327	.1
325	.1
323	.1
321	.1
320	.1
309	.1
308	.5
307	4.2
306	.0
305	.3
295	.1
293	.3
291	.1
283	.1
282	.0
281	.1
280	.0
279	.2
278	0
277	1
276	1
275	0
275	1
274	1
273	2
272	4 1
271	1
270	2
269	1
268	5
267	2
267	1
266	1
265	9
263	1
261	1
260	1
259	2
258	5
257	6.5
256	.8
255	2 3
254	1
253	0
252	3
251	2
250	0
249	1
243	5
242	6 2
241	0
240	1 4
237	0
236	2
235	1
230	0
229	.0
224	1
223	2
211	1
210	1
209	5
208	1
207	7
205	0
203	0
202	0
201	0
200	1
195	2
194	1
193	3
192	1
191	.1
189	.1
185	.0
183	.0
182	.1
181	.0
180	.0
179	.6
178	.0
177	.1
175	.0
171	.1
168	.0
167	.4
165	.8
164	.1
163	.2
162	.1
157	.1
156	.1
155	.1
155	.1
154	.1
153	.1
152	.2
152	.1
151	.6
150	.3
149	1.3
148	.1
147	.1
147	.0
146	1.6
145	6.7
144	1.0
143	3.3
142	.5
141	.2
140	.1
139	.0
139	.1
138	.0
137	.2
136	.1
135	.0
135	.1
134	.1
133	.2
132	.3
131	.4
130	4.5
129	.6
128	.1
128	1.0
127	.0
127	4.2
126	.0
126	.1
125	.1
125	.1
124	.1
123	.0
123	.2
122	.1
121	.1
120	.0
120	.3
119	.1
118	.0
117	.0
116	.2
115	6.4
113	.1
113	2.2
112	.1
112	.0
111	.1
110	.1
109	.1
108	.0
107	.1
106	.1
105	.1
104	.1
103	.0
101	.0
99	.1
99	.1
98	.1
97	.2
96	.1
95	.2
94	.1
93	.1
92	.0
91	.1
90	.0
89	.1
85	.2
84	.1
83	.2
82	.1
81	.4
80	.0
79	.1
78	.0
77	.1
76	.1
75	.1
74	.0
73	.1
71	.3
70	.2
69	.7
68	.1
67	.1
65	.1
63	.0
59	.1
58	.1
57	1.3
56	.2
55	.4
54	.1
53	.1
51	.1
50	.0
44	.2
43	.4
42	.1
41	.8
40	.0
39	.3
38	.0
29	.4
29	.0
28	.1
28	.1
27	.3
26	.1
17	.1

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